PB-250 585

# SO2 ABATEMENT FOR STATIONARY SOURCES IN JAPAN

Jumpei Ando, et al

PEDCo-Environmental Specialists,
Incorporated

Prepared for:

Industrial Environmental Research Laboratory

January 1976

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

## TECHNICAL REPORT DATA
*(Please read Instructions on the reverse before completing)*

1. REPORT NO. EPA-600/2-76-013a

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE $SO_2$ Abatement for Stationary Sources in Japan

5. REPORT DATE January 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) Jumpei Ando (Chuo University, Tokyo, Japan) and Gerald A. Isaacs

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
PEDCo-Environmental Specialists, Inc.
Suite 13, Atkinson Square
Cincinnati, Ohio 45246

10. PROGRAM ELEMENT NO. 1AB013; ROAP 21ACX-130

11. CONTRACT/GRANT NO. 68-02-1321, Task 6

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED Subtask Final; 7/74-3/75

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT The report describes the status of desulfurization technology in Japan up to January 1975, with emphasis on the recovery of SO2 in lime/limestone based processes. It discusses the current status of desulfurization technologies, including hydrodesulfurization of oil, decomposition of residual oil, gasification of coal and oil, and flue gas desulfurization (FGD). Major Japanese FGD processes are examined in detail. Technical and economic aspects of the systems are discussed, and the processes are evaluated for potential U.S. application. Principal by-products of the various systems are discussed. The report also contains background information on energy usage, fuel resources, and projected pollutant abatement requirements in Japan.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group | |
|---|---|---|---|---|
| Air Pollution | Residual Oils | Air Pollution Control | 13B | |
| Sulfur Dioxide | Decomposition | Stationary Sources | 07B | |
| Calcium Oxides | Coal | Japan | | |
| Limestone | Gasification | Hydrodesulfurization | 08G | 13H,07A |
| Fossil Fuels | Flue Gases | Fuel Resources | 21D | 21B |
| Oils | Desulfurization | | 11H | 07D |
| Scrubbers | Energy | | | |

18. DISTRIBUTION STATEMENT Unlimited

19. SECURITY CLASS (This Report) Unclassified

20. SECURITY CLASS (This page) Unclassified

21. NO. OF PAGES 195

22. PRICE 7.50

EPA Form 2220-1 (9-73)

079030

PB 250 585

EPA-600/2-76-013a
January 1976

Environmental Protection Technology Series

[illegible]

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

## RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

## EPA REVIEW NOTICE

**This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.**

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-76-013a

# $SO_2$ ABATEMENT
# FOR STATIONARY SOURCES
# IN JAPAN

by

Jumpei Ando

Chuo University
Kasuga, Bunkyo-ku, Tokyo

and

G.A. Isaacs

PEDCo-Environmental Specialists, Inc.
Suite 13, Atkinson Square
Cincinnati, Ohio 45246

Contract No. 68-02-1321, Task 6
ROAP No. 21ACX-130
Program Element No. 1AB013

EPA Task Officer: Norman Kaplan

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

January 1976

# FOREWORD

This report describes recent developments in desulfurization technology in Japan up to January 1975, with emphasis on recovery of $SO_2$ in lime/limestone-based processes. Section 1 provides background information on energy usage in Japan; currently available fuel resources, including imports; regulations limiting ambient concentrations and emissions of $SO_2$; and projected requirements for abatement measures to meet the regulations.

Section 2 reviews briefly the current status of desulfurization technologies, including hydrodesulfurization of oil, decomposition of residual oil, gasification of oil and coal, and flue gas desulfurization (FGD).

The next three sections examine in detail the major FGD processes operating in Japan, in the categories of wet lime/limestone processes (Section 3), indirect lime/limestone processes (Section 4), and other processes for $SO_2$ recovery (Section 5).

Section 6 describes the major by-products of the various processes, and Section 7 summarizes some of the technical and economic aspects of the FGD systems, with evaluation of their potential for application in the United States.

# CONVERSION FACTORS AND ABBREVIATIONS

## CONVERSION FACTORS

The metric system is used in this report. Following are some factors for conversion between metric and English systems:

1 m (meter) = 3.3 feet

1 $m^3$ (cubic meter) = 35.3 cubic feet

1 t (metric ton) = 1.1 short tons

1 kg (kilogram) = 2.2 pounds

1 liter = 0.26 gallon

1 kl (kiloliter) = 6.29 barrels

The capacity of flue gas desulfurization plants is expressed in $Nm^3/hr$ (normal cubic meters per hour)

1 $Nm^3/hr$ = 0.59 standard cubic foot per minute

L/G ratio (liquid/gas ratio) is expressed in liters/$Nm^3$.

1 liter/$Nm^3$ = 7.4 gallons/thousand standard cubic feet

For monetary conversions, the exchange rate of 1 dollar = 300 yen is used.

## ABBREVIATIONS

| | |
|---|---|
| FGD | Flue gas desulfurization |
| HDS | Hydrodesulfurization |
| BPSD | Barrels per stream day |
| MW | Megawatts |
| L/G | Liquid/gas ratio (see above) |
| $Nm^3/hr$ | Normal cubic meters per hour |

## TABLE OF CONTENTS

| | | Page |
|---|---|---|
| FOREWORD | | iii |
| CONVERSION FACTORS AND ABBREVIATIONS | | v |
| LIST OF FIGURES | | xi |
| LIST OF TABLES | | xv |
| 1. | ENERGY USAGE, FUEL RESOURCES, AND ENVIRONMENTAL STANDARDS | 1-1 |
| | Energy Usage | 1-1 |
| | Oil Supplies and Sulfur Content | 1-2 |
| | Ambient and Emission Standards for $SO_2$ | 1-4 |
| | Requirements for $SO_2$ Abatement | 1-6 |
| 2. | STATUS OF DESULFURIZATION TECHNOLOGIES | 2-1 |
| | Introduction | 2-1 |
| | Status of Hydrodesulfurization (HDS) of Heavy Oils | 2-2 |
| | Decomposition of Residual Oil and Gasification Desulfurization | 2-5 |
| | Status of Flue Gas Desulfurization | 2-11 |
| 3. | WET LIME-LIMESTONE PROCESSES FOR $SO_2$ RECOVERY | 3-1 |
| | Introduction | 3-1 |
| | Mitsubishi-JECCO Lime-Limestone Process | 3-8 |
| | Chemico-Mitsui and Mitsui Miike Lime-Limestone Processes | 3-22 |

TABLE OF CONTENTS (continued)

Page

Babcock-Hitachi Process 3-30

Chuba-MKK Process 3-35

Kobe Steel Calcium Chloride Process 3-37

Sumitomo-Fuji Kasui Process 3-42

Other Wet Lime/Limestone Processes 3-45

4. INDIRECT LIME-LIMESTONE PROCESS 4-1

Introduction 4-1

Showa Denko Sodium-Limestone Process 4-4

Kureha-Kawasaki Sodium-Limestone Process 4-9

Nippon Kokan Ammonia Scrubbing Process 4-14

Chiyoda Dilute Sulfuric Acid Process 4-25

Dowa Aluminum Sulfate Process 4-34

Kurabo Ammonium Sulfate Lime Process 4-42

Other Indirect Lime/Limestone Processes 4-48

5. OTHER PROCESSES FOR $SO_2$ RECOVERY 5-1

Introduction 5-1

Wellman-MKK Sodium Process 5-3

Onahama-Tsukishima Magnesium Process 5-11

Other Wet Processes 5-14

Shell Copper Oxide Process 5-19

Other Dry Processes 5-25

6. BY-PRODUCTS 6-1

Introduction 6-1

Sulfuric Acid 6-3

## TABLE OF CONTENTS (continued)

Page

Elemental Sulfur 6-5

Ammonium Sulfate 6-6

Calcium Sulfite 6-7

Gypsum 6-8

7. COMPARATIVE EVALUATION 7-1

Wastewater 7-1

Economics 7-4

Technical Evaluation 7-6

Potential for Application in the U.S.A. 7-10

REFERENCES

# LIST OF FIGURES

| Figure | | Page |
|---|---|---|
| 2-1 | Material Balance for Residual Oil Decomposition by the Flexicoking Process | 2-7 |
| 2-2 | Material Banance of the Kureha Process | 2-7 |
| 2-3 | Flowsheet of Kureha Process | 2-9 |
| 3-1 | Schematic Flowsheet of Wet Lime/Limestone Process | 3-3 |
| 3-2 | Flowsheet of Mitsubishi-JECCO Lime/Limestone Process. | 3-12 |
| 3-3 | Single-Tower System | 3-14 |
| 3-4 | Onahama Plant, Onahama Smelting | 3-16 |
| 3-5 | Kainan Plant, Kansai Electric | 3-16 |
| 3-6 | Yokosuke Plant, Tokyo Electric | 3-17 |
| 3-7 | Tower Mill at Yokosuka Plant | 3-17 |
| 3-8 | By-Product Gypsum at Kainan Plant, Kansai Electric | 3-21 |
| 3-9 | Influence of Slurry pH on Oxidation Rate and $HSO_3^-$ Concentration | 3-21 |
| 3-10 | Omuta Plant, Mitsui Aluminum | 3-23 |
| 3-11 | Sludge Pond at Omuta Plant, Mitsui | 3-23 |
| 3-12 | Flowsheet of Chemico-Mitsui Lime Process | 3-26 |
| 3-13 | X-Ray Diffraction Pattern of Sludge from Scrubber | 3-27 |
| 3-14 | Flowsheet of Mitsui Miike Limestone-Gypsum Process | 3-28 |

## LIST OF FIGURES (continued)

| | | Page |
|---|---|---|
| 3-15 | Effect of Catalyst on $SO_2$ Removal Efficiency | 3-28 |
| 3-16 | Flowsheet of Babcock-Hitachi Limestone-Gypsum Process | 3-32 |
| 3-17 | Mizushima Plant, Chugoku Electric | 3-24 |
| 3-18 | Flowsheet of CM Process | 3-36 |
| 3-19 | Flowsheet of Kobe Steel Process | 3-39 |
| 3-20 | Solubility of Lime in Calcium Chloride Solution | 3-40 |
| 3-21 | Vapor Pressure of $SO_2$ | 3-40 |
| 3-22 | L/G and $SO_2$ Removal Efficiency | 3-40 |
| 3-23 | Vapor Pressure of $H_2O$ | 3-40 |
| 3-24 | Simplified Flowsheet of Moretana Process | 3-44 |
| 3-25 | Flowsheet of Chemico-IHI Process | 3-47 |
| 4-1 | Flowsheet of Showa Denko Process | 4-5 |
| 4-2 | Scrubbers | 4-6 |
| 4-3 | By-Product Gypsum | 4-6 |
| 4-4 | Availability of Chiba Plant Since 1973 | 4-7 |
| 4-5 | Flowsheet of Kureha-Kawasaki Process | 4-10 |
| 4-6 | Shinsendai Plant, Tohoku Electric | 4-11 |
| 4-7 | Schematic Flowsheet - Nippon Kokan Ammonia Scrubbing Process | 4-15 |
| 4-8 | Jinkoshi Scrubber | 4-17 |
| 4-9 | Ammonia-Lime Process | 4-17 |
| 4-10 | Nippon Kokan Ammonia-Lime Process | 4-18 |
| 4-11 | Jinkoshi-NKK Type Scrubber | 4-20 |
| 4-12 | Flowsheet of Chiyoda Process | 4-27 |

## LIST OF FIGURES (continued)

| Figure | | Page |
|---|---|---|
| 4-13 | Temperature and Oxidation Ratio with Catalysts | 4-29 |
| 4-14 | Catalyst Consumption | 4-29 |
| 4-15 | Liquid/Gas Ratio and $SO_2$ Removal | 4-30 |
| 4-16 | Double-Cylinder Type Reactor | 4-30 |
| 4-17 | Toyama Plant, Hokuriku Electric | 4-32 |
| 4-18 | Toyama Plant, Hokuriku Electric | 4-32 |
| 4-19 | Abosi Plant, Daicel Co. | 4-33 |
| 4-20 | $SO_2$ Absorbing Capacity of the Liquors | 4-36 |
| 4-21 | Boiling Point of the Liquor Containing $SO_2$ | 4-36 |
| 4-22 | $SO_2$ Absorbing Capacity of Dilute Liquors | 4-36 |
| 4-23 | Flowsheet of Dowa Aluminum Sulfate - Limestone Process | 4-38 |
| 4-24 | Okayama Plant, Dowa Mining Absorbers, Oxidizers | 4-40 |
| 4-25 | Okayama Plant, Dowa Mining | 4-40 |
| 4-26 | Relationship of $SO_2$ + $HSO_3$ Concentration to Partial Pressure of $SO_2$ | 4-43 |
| 4-27 | $SO_2$ Removal Efficiency at the Test Unit | 4-43 |
| 4-28 | Flowsheet of Kurabo Ammonium Sulfate Gypsum Process | 4-45 |
| 4-29 | Oxidation Rate of Sulfite Ion | 4-45 |
| 4-30 | Tamashima Plant, Jurarey | 4-47 |
| 4-31 | Flowsheet of Tsukishima Double-Alkali Process | 4-50 |
| 5-1 | Flowsheet of the Wellman-MKK Process | 5-4 |
| 5-2 | Layout of the FGD Plant at Nishinagoya Station | 5-5 |
| 5-3 | Nishinagoya Plant, Chuba Electric | 5-9 |

## LIST OF TABLES

| Table | | Page |
|---|---|---|
| 1-1 | Possible Supplies of Primary Energies | 1-2 |
| 1-2 | Imports of Crude Oil by Sources | 1-3 |
| 1-3 | Imported Crude Oil and Average Sulfur Contents | 1-3 |
| 1-4 | Heavy Oil Shipments and Average Sulfur Contents | 1-4 |
| 1-5 | Values of k | 1-5 |
| 1-6 | Capacity of Power Generation in Japan | 1-6 |
| 1-7 | Use of Fuels by Nine Major Power Companies | 1-7 |
| 1-8 | FGD of Fuel Oil Required to Attain 0.04 ppm $SO_2$ in Environment | 1-8 |
| 2-1 | Hydrodesulfurization Plants Built by 1971 | 2-3 |
| 2-2 | Hydrodesulfurization Plants Completed Between 1972 and 1974 | 2-4 |
| 2-3 | Prices of Heavy Oils | 2-5 |
| 2-4 | Hydrodesulfurization Plants to be Completed After 1974 | 2-6 |
| 2-5 | $SO_2$ Recovery Processes and Plant Capacities | 2-12 |
| 3-1 | Major Sulfur Dioxide Scrubbing Installations in Japan | 3-2 |
| 3-2 | Example of Operation Parameters of FGD Plants By-Producing Gypsum and Calcium Sulfite | 3-4 |
| 3-3 | Amounts of Wastewater and Gypsum | 3-9 |
| 3-4 | Wet Lime-Limestone Process Plants Using the Mitsubishi-JECCO Process | 3-11 |

# LIST OF TABLES (continued)

| Table | | Page |
|---|---|---|
| 3-5 | Operation Data: Kansai and Tokyo Plants | 3-18 |
| 3-6 | Plants Using the Mitsui Miike Limestone | 3-25 |
| 3-7 | Example of the Composition of By-Product | 3-29 |
| 3-8 | Plants Using the Babcock-Hitachi Process | 3-31 |
| 3-9 | Plants Using the Moretana Process | 3-42 |
| 4-1 | Indirect Lime-Limestone Process | 4-2 |
| 4-2 | Plants Using the Kureha-Kawasaki Process | 4-9 |
| 4-3 | Annual Requirements for Operation of the Nippon Kokan Processes | 4-22 |
| 4-4 | Estimated Cost of NKK Type Ammonium Sulfate System | 4-23 |
| 4-5 | Estimated Cost of NKK Type Ammonia-Lime System | 4-24 |
| 4-6 | Commercial Plants Using the Chiyoda Process | 4-26 |
| 4-7 | Size of Towers Required for the Chiyoda Process | 4-28 |
| 4-8 | Composition of Solutions in Figures 4.20 and 4.21 | 4-35 |
| 4-9 | Plants Using the Kurabo Ammonium Sulfate Lime Process | 4-42 |
| 4-10 | Minimum L/G Ratio Required for 95 Percent $SO_2$ Removal | 4-44 |
| 4-11 | Design Base of $SO_2$ Absorber | 4-44 |
| 4-12 | Estimated Costs of Kurabo Process | 4-29 |
| 5-1 | Sulfur Dioxide Scrubbing Installations in Japan that By-Produce Sulfuric Acid and Sulfur | 5-2 |
| 5-2 | Specifications for Main Equipment | |

## LIST OF TABLES (continued)

| Table | | Page |
|---|---|---|
| 6-1 | Sources and Uses of Sulfuric Acid in Japan | 6-4 |
| 6-2 | Supply of and Demand for Sulfur | 6-5 |
| 6-3 | Blending of Materials | 6-17 |
| 6-4 | Properties of Gypsum and GPC | 6-17 |
| 7-1 | Wastewater from FGD Plants | 7-2 |

# 1. ENERGY USAGE, FUEL RESOURCES, AND ENVIRONMENTAL STANDARDS

## ENERGY USAGE

Energy usage in Japan has increased rapidly over recent years and has been heavily dependent on imported oil. The oil crisis of late 1973 and the serious inflation resulting from it have strongly affected Japan's energy and environmental policies. Strenuous efforts are now being applied to development of atomic energy and to the import of LNG and coal. Use of imported crude oil, which has constituted more than 70 percent of the total energy usage in Japan and has been the major source of $SO_2$ emissions, is expected to continue increasing at an annual rate of 6 to 7 percent, as against increases of 20 to 30 percent in the past. Although technologies for desulfurization of heavy oil have progressed steadily, construction of many plants planned for gasification of oil has been postponed or abandoned, mainly because of inflation; in recent months the already high investment cost for such plants has more than doubled.

Annual increases in energy consumption in Japan averaged 11 percent during the past several years and are expected to continue at about 6 percent for a few years to come. An energy supply plan has been proposed recently by the Energy Research Committee of the Ministry of International Trade and Industry (MITI) (Table 1-1). During the period from 1972 to 1985, the amount of imported oil will double, but its proportion in total energy usage will decrease from 75 to 61 percent. Over the same period the sum of domestic energies and atomic power will increase in the range of 14 to 20 percent.

Table 1-1. POSSIBLE SUPPLIES OF PRIMARY ENERGIES

| | 1972 | 1980 | | 1985 | |
|---|---|---|---|---|---|
| | | min. | max. | min. | max. |
| Hydroelectric power, $10^3$ MW | 20 | 27 | 29 | 29 | 33 |
| Geothermal energy, $10^3$ MW | 0.03 | 0.4 | 1 | 1 | 6 |
| Domestic oil and gas, $10^6$ kl | 3.7 | 5.5 | 11 | 13 | 30 |
| Domestic coal, $10^6$ t | 28 | 20 | 20 | 20 | 20 |
| Atomic power, $10^3$ MW | 1.8 | 22 | 25 | 50 | 70 |
| Imported LNG, $10^6$ t | 1 | 24 | 29 | 36 | 62 |
| Imported coal, $10^6$ t | 50 | 94 | 104 | 111 | 121 |
| Imported oil, $10^6$ kl | 270 | 400 | 450 | 500 | 600 |

Per-capita energy consumption in Japan was one-fifth that in the United States in 1965 and one-third in 1972. Consumption per acre of level land is now about 8 times that in the U.S. and may be the highest in the world; this high level of energy consumption presents increasingly serious problems of energy supply and environmental protection.

## OIL SUPPLIES AND SULFUR CONTENT

Most of the oil imported to Japan is in the form of crude oil (Table 1-2). About 80 percent of the crude oil comes from the Middle East and is rich in sulfur. In addition, some heavy fuel oil is being imported. Even though the average sulfur content of imported crude oil decreased from 1.82 percent in 1968 to 1.50 percent in 1972, the total amount of sulfur in imported oil reached nearly 4 million tons in 1972 (Table 1-3).

In Japan, most of the crude oil is treated by topping (atmospheric distillation). The residual oil from topping, known as "heavy oil", is used for fuel. From 100 parts crude, 55 parts heavy oil is obtained on the average. Approximately 90 percent of the sulfur in crude remains in the heavy oil. The sulfur content of heavy oil from Khafji

Table 1-2. IMPORTS OF CRUDE OIL BY SOURCES[1]

(in $10^6$ kiloliters; 1 kl = 6.29 bbl)

| Source | 1969 | 1970 | 1971 | 1972 |
|---|---|---|---|---|
| Middle East total | 150.4 | 169.2 | 182.2 | 190.4 |
| Saudi Arabia | 29.0 | 28.6 | 30.0 | 40.8 |
| Kuwait | 14.3 | 18.2 | 19.7 | 21.7 |
| Neutral Zone | 18.4 | 18.8 | 18.8 | 19.3 |
| Iran | 75.2 | 84.8 | 91.8 | 87.5 |
| Others | 13.6 | 18.8 | 22.1 | 21.0 |
| Southeast Asia | 16.7 | 23.5 | 25.1 | 31.0 |
| U.S.S.R. | 0.6 | 0.6 | 0.5 | 0.4 |
| Others | 0.9 | 2.1 | 3.6 | 5.5 |
| Total | 168.6 | 195.3 | 211.4 | 227.3 |

Table 1-3. IMPORTED CRUDE OIL AND AVERAGE SULFUR CONTENTS

| | 1968 | | 1970 | | 1972 | |
|---|---|---|---|---|---|---|
| | Amount, $10^6$kl | Ratio, % | Amount, $10^6$kl | Ratio, % | Amount, $10^6$kl | Ratio, % |
| Low sulfur | 16.0 | 11.2 | 36.6 | 18.7 | 48.8 | 21.4 |
| Medium sulfur | 73.3 | 51.5 | 117.7 | 60.3 | 135.3 | 59.3 |
| High sulfur | 52.6 | 37.3 | 41.0 | 21.0 | 44.0 | 19.3 |
| Total | 141.9 | 100.0 | 195.3 | 100.0 | 228.1 | 100.0 |
| Average sulfur, % | 1.82 | | 1.58 | | 1.50 | |

crude can be as high as 4 percent. Hydrodesulfurization of heavy oil has been carried out since 1968. The average sulfur contents and the amounts of heavy oil shipped by refineries are shown in Table 1-4.

Table 1-4. HEAVY OIL SHIPMENTS AND AVERAGE SULFUR CONTENTS

| | 1967 | 1969 | 1971 | 1973 |
|---|---|---|---|---|
| Amount, $10^6$ kl | 70.0 | 82.6 | 109.3 | 134.6 |
| Sulfur, % | 2.50 | 2.06 | 1.74 | |

AMBIENT AND EMISSION STANDARDS FOR $SO_2$

Regulations of $SO_2$ emissions have become more stringent with time. The ambient standard for $SO_2$ concentration was changed from 0.05 ppm (yearly average) to 0.04 ppm (daily average) in May 1973. By the new standard, the hourly average should not exceed 0.1 ppm and the daily average should not exceed 0.04 ppm.

The emission standard is given by the following equation:

$$Q = k \times 10^{-3} H_e^2$$

Q: Amount of sulfur oxides, $Nm^3$/hr (1 $Nm^3$/hr = 0.59 scfm)
k: The value shown in Table 1-5.
He: Effective height of stack, meters (1 meter = 3.3 ft)

In an effort to reduce total $SO_2$ emissions by 11 percent from the previous year, the k values, which determine permissible emissions, were also changed, as shown in Table 1-5.

Table 1-5. VALUES OF k

| | For existing plants | | For new plants | |
|---|---|---|---|---|
| | 1972 | 1974 | 1972 | 1974 |
| Tokyo, Osaka, etc. | 6.42 | 3.50 | 2.92 | 1.17 |
| Chiba, Fuji, etc. | 7.59 | 4.67 | 3.50 | 1.75 |
| Omuta, Ube, etc. | 9.34 | 6.42 | 5.26 | 2.34 |
| Kyoto, Toyama, etc. | | 8.76 | 5.26 | 2.34 |

For a new 500 MW plant, to meet the standards in the Tokyo and Osaka areas, the sulfur content of oil must be below 0.3 percent, even with a 200-meter stack. The new emission standard, however, has proved unsatisfactory in keeping the ambient concentrations below 0.04 ppm in large cities and heavily industrialized areas. To attain the environmental standard by March 1978, the central government issued a new regulation in November 1974 to restrict the total amount of $SO_2$ emissions in the following eleven polluted areas: (1) Tokyo (2) Chiba (3) Yokohama, Kawasaki (4) Fuji (5) Nagoya (6) Handa (7) Yokkaichi (8) Osaka, Saki (9) Kobe, Amagasaki (10) Kurashiki, Mizushima (11) Kitakyushu. The new regulation applies to plants using more than 0.1 to 1.0 kiloliter of oil per hour (0.4 to 4.0 MW equivalent). A certain number between 0.1 and 1.0 is to be assigned to each prefecture by the Governor, and the amount of allowable $SO_2$ is calculated by one of the following formulas, to be selected by each prefecture.

$$Q = a \times W^b \qquad (1)$$

Q: Amount of allowable $SO_2$
a: A constant to ensure $SO_2$ abatement
W: Amount of fuel used by each plant
b: A constant between 1.00 and 0.80 to be selected by the prefectural governor

$$Q = Q_o \times C_m/C_{m_o} \qquad (2)$$

$C_m$: Maximum ground-level concentration to ensure $SO_2$ abatement

$C_{m_o}$: Maximum ground-level concentration due to each plant

$Q_o$: Amount of $SO_2$ being emitted.

The amount of $SO_2$ allowed for each plant is being calculated by each prefecture and will be determined by the middle of 1975. The new regulation requires substantial reduction of $SO_2$ emission. For areas to which the new regulation does not apply, $SO_2$ emission limits will be specified by the k value, which will become lower year by year.

## REQUIREMENTS FOR $SO_2$ ABATEMENT

The capacity of electric power generation in Japan is shown in Table 1-6. The total capacity has increased remarkably, approaching 100,000 MW in 1973. The use of coal decreased during the last 5 years, while oil consumption more than doubled. Now nearly 70 percent of Japan's total electric power is generated by oil-firing.

Table 1-6. CAPACITY OF POWER GENERATION IN JAPAN
(Thousands of megawatts)

| | 1967 | 1969 | 1971 | 1973 |
|---|---|---|---|---|
| Hydroelectric | 17.1 | 19.3 | 20.2 | 22.6 |
| Thermal (oil)[a] | 18.7 | 25.2 | 41.5 | 64.2 |
| Thermal (coal) | 13.4 | 14.4 | 13.6 | 6.3 |
| Atomic | 0.2 | 0.5 | 1.3 | 2.2 |

[a] Includes a minor amount of gas-firing.

The fuels used in 1972 and 1973 by the nine major power companies, which account for more than 70 percent of Japan's total power generation, are listed in Table 1-7. The power companies have been recently planning to use large amounts of low-sulfur fuels such as crude oil, naphtha, and LNG to replace heavy oil. Oil companies, which oppose the plan of the power companies because it would require drastic changes in oil refining, have been trying to reduce the sulfur content of heavy oil by hydrodesulfurization and also to develop gasification processes.

Flue gas desulfurization has so far been used mainly by industries other than power companies, because the industries have had difficulty in obtaining low-sulfur fuels. The use of flue gas desulfurization by the power companies represented only about 400 MW in 1973 but will probably increase to 10,000 MW in 1977.

Table 1-7. USE OF FUELS BY NINE MAJOR POWER COMPANIES[a]

| | 1972 | | 1973 | |
|---|---|---|---|---|
| | Amount | S, % | Amount | S, % |
| Coal, $10^6$ t | 6.4 | 0.55 | 4.2 | 0.52 |
| Heavy oil, $10^6$ kl | 30.4 | 1.01 | 31.6 | 0.82 |
| Crude oil, $10^6$ kl | 17.8 | 0.89 | 23.0 | 0.59 |
| Naphtha, $10^6$ kl | 0.2 | 0.12 | 2.4 | 0.09 |
| LNG, $10^6$ kl | 0.7 | 0.00 | 1.3 | 0.00 |
| LGL, $10^6$ kl | 0.0 | | 0.7 | 0.04 |
| Natural gas, $10^8$ $Nm^3$ | 1.8 | 0.00 | 2.3 | 0.00 |
| Coke oven gas, $10^8$ $Nm^3$ | 2.6 | 0.80 | 4.1 | 0.65 |

[a] These companies produce 71 percent of Japan's total electric power.

Table 1-8 shows an estimation by MITI of the amount of fuel oil that must be subjected to flue gas desulfurization to attain the ambient standard of 0.04 ppm $SO_2$, assuming that the oil contains 2 percent sulfur on the average and 90 percent of the $SO_2$ in the flue gas is removed. In 1975, 1976, and 1977, the oil so treated will amount to 1637, 2362, and 2720 x $10^4$ kl, respectively; these values are equivalent to power capacities of 9000, 13,000 and 15,000 MW. In addition, other waste gases, such as those from sulfuric acid plants, Claus furnaces, sintering plants, and smelters will be treated by desulfurization.

Table 1-8. FGD OF FUEL OIL REQUIRED TO ATTAIN 0.04 ppm $SO_2$ IN ENVIRONMENT

($10^4$ kl oil)

| | 1973 | 1974 | 1975 | 1976 | 1977 |
|---|---|---|---|---|---|
| Power | 141 | 450 | 625 | 1027 | 1166 |
| Chemical industry | 89 | 184 | 349 | 490 | 568 |
| Paper industry | 143 | 239 | 371 | 413 | 433 |
| Petroleum industry | 43 | 43 | 133 | 207 | 237 |
| Metal industry | 30 | 36 | 46 | 51 | 53 |
| Textile industry | 11 | 17 | 46 | 92 | 174 |
| Ceramic industry | 20 | 57 | 67 | 81 | 90 |
| Total | 477 | 1026 | 1637 | 2361 | 2721 |

# 2. STATUS OF DESULFURIZATION TECHNOLOGIES

## INTRODUCTION

Among various ways of desulfurization, hydrodesulfurization (HDS) of heavy oil has been adopted widely since 1968. In 1973 about 30 percent of all heavy oil underwent HDS, by-producing about 700,000 tons of elemental sulfur. The desulfurized oil and the imported low-sulfur oils have been used mainly by power companies for utility boilers. Other industries have had difficulty in obtaining low-sulfur fuel and have been practicing flue gas desulfurization (FGD).

The easiest method of FGD, sodium scrubbing to by-produce sodium sulfite salable to paper mills, was first to become popular. FGD processes that by-produce gypsum and sulfuric acid became popular after 1972 as the supply of sodium sulfite filled the demand.

Generally speaking, FGD costs less than does HDS, which requires large amounts of catalyst and hydrogen. For users of fuel, it is easier to burn desulfurized oil than to operate FGD plants. If oversupply of desulfurization by-products were to occur, elemental sulfur from HDS offers advantages over other by-products. For these reasons, use of both HDS and FGD will continue to grow.

In 1972 and 1973, desulfurization of heavy oil by gasification was considered promising because sulfur in oil may be reduced to below 0.2 percent equivalent, a reduction that may be needed in future but seems difficult to attain by HDS. Many companies, mostly oil companies, planned to construct commercial gasification plants. Most of the plans, however, have been given up or postponed recently, for several reasons: (1) the high investment costs, which have been further raised by inflation; (2) the poor ability of the gasifiers to follow changes in operating loads of utility boilers; and (3) the recent development of HDS technology, which has made it possible to reduce sulfur content to 0.3 percent or even lower. It seems more rational to decompose residual oil from vacuum distillation of heavy oil that cannot be treated by HDS than to gasify heavy oil. At present two commercial plants are under construction to decompose residual oil to gas oil, gas, and coke or pitch.

Although gasification of coal was performed many years ago, development of this process was abandoned as oil became much cheaper than coal. With the present drastic increase in oil prices, tests of coal gasification have been resumed.

## STATUS OF HYDRODESULFURIZATION (HDS) OF HEAVY OIL

Most Japanese oil refiners have installed HDS plants since 1968 (Tables 2-1 and 2-2). There are two methods of HDS: (1) Vacuum gas-oil HDS, in which the vacuum gas-oil obtained by the vacuum distillation of heavy oil is desulfurized to about 0.2 percent sulfur. This treatment is fairly easy but the residual oil from the distillation contains approximately 40 percent of the heavy oil which is rich in sulfur and metallic impurities that cannot be desulfurized. (2) Topped-crude HDS, in which heavy oil is directly treated. It is difficult to reduce sulfur content below 1 percent by this process; however, since 1 percent sulfur oil has become unsatisfactory for use in many places, several oil companies, including Idemitsu Kosan and Mitsubishi Oil, have started to build new plants to reduce sulfur to 0.3 percent or less by using new catalysts and two reactors in series. Hydrogen consumption required to decrease sulfur from 1.0 to 0.3 percent is nearly twice that required to reduce it from 1.7 to 1.0 percent.

## Table 2-1. HYDRODESULFURIZATION PLANTS BUILT BY 1971

| Refiner | Plant site | Process | Completed | Capacity per day<br>Oil, BPSD | Capacity per day<br>Sulfur, tons |
|---|---|---|---|---|---|
| Idemitsu Kosan | Chiba | UOP[a] | 1967 | 40,000 | 265 |
| Fuji Oil | Sodegaura | CRC | 1968 | 23,000 | 100 |
| Ota Nenryo | Wakayama | ER & E | 1968 | 25,000 | 180 |
| Daikyo Oil | Umaokoshi | Gulf | 1969 | 17,500 | 110 |
| Nippon Oil | Negishi | CRC | 1969 | 40,000 | 190 |
| Showa Oil | Kawasaki | Shell | 1969 | 16,000 | 66 |
| Kyushu Oil | Oita | Shell | 1969 | 14,000 | 55 |
| Mitsubishi Oil | Mizushima | UOP | 1969 | 30,000 | 100 |
| Maruzen Oil | Chiba | Union | 1969 | 35,000 | 165 |
| Seibu Oil | Yamaguchi | Shell | 1969 | 4,000 | 28 |
| Nippon Mining | Mizushima | Bulf[a] | 1970 | 27,760 | 165 |
| Koa Oil | Marifu | CRC | 1970 | 8,000 | 39 |
| General Oil | Sakai | ER & E | 1970 | 31,000 | 73 |
| Kashima Oil | Kashima | UOP[a] | 1970 | 45,000 | 265 |
| Daikyo Oil | Umaokoshi | Gulf | 1970 | 17,500 | 77 |
| Kansai Oil | Sakai | ER & E | 1971 | 20,000 | 88 |
| Koa Oil | Osaka | CRC | 1971 | 12,000 | 55 |
| Toa Nenryo | Kawasaki | ER & E | 1971 | 51,000 | 220 |
| Total | | | | 456,760 | 2,241 |

[a] Topped-crude HDS processes; other processes are vacuum gas-oil HDS.

Table 2-2. HYDRODESULFURIZATION PLANTS COMPLETED BETWEEN 1972 AND 1974

| Refiner | Plant site | Process | Year of completion | Capacity oil, BPSD |
|---|---|---|---|---|
| Nippon Oil | Negishi | CRC | 1972 | 28,000 |
| Idemitsu Kosan | Himeji | Gulf[a] | 1972 | 40,000 |
| Kyokuto Petroleum | Chiba | UOP | 1972 | 60,000 |
| Toa Nenryo | Kawasaki | ER & E | 1972 | 9,000 |
| Asia Kyoseki | Sakaide | CRC | 1972 | 15,000 |
| Kyushu Oil | Oita | UOP | 1972 | 25,000 |
| Showa Yokkaichi Oil | Yokkaichi | Shell | 1972 | 35,000 |
| Seibu Oil | Yamaguchi | Shell | 1972 | 1,000 |
| Nippon Oil | Muroran | CRC | 1973 | 40,000 |
| Toa Oil | Nagoya | CRC | 1973 | 30,000 |
| Nippon Mining | Mizushima | Gulf[a] | 1974 | 3,240 |
| Toa Oil | Nagoya |  | 1974 | 37,000 |
| Kansai Oil | Sakai | ER & E | 1974 | 2,000 |
| Showa Yokkaichi Oil | Yokkaichi | Shell | 1974 | 5,000 |
| Mitsubishi Oil | Mizushima | UOP[a] | 1974 | 45,000 |
| Total |  |  |  | 375,240 |

[a] Topped-crude HDS; other processes are vacuum gas-oil HDS.

Cost of desulfurization, including both fixed and running costs to reduce sulfur in heavy oil from 4 to 1 percent, was about $7 (¥2100)/kl in 1972 and has nearly tripled for plants to be constructed. Considerable additional cost will be required to reduce sulfur to 0.3 percent or below. The prices of heavy oils of various sulfur contents are shown in Table 2-3.

Table 2-3. PRICES OF HEAVY OILS
(Dollars per kiloliter)

| Grade | | 1972 | Late 1974 |
|---|---|---|---|
| High sulfur | (S = 2.5%) | 17-19 | 55-60 |
| Medium sulfur | (S = 1.0%) | 22-24 | 75-85 |
| Low sulfur | (S = 0.3%) | | 85-95 |

Because of the large difference between the prices of high- and low-sulfur oils and because of the new severe regulations on $SO_2$ emission, many HDS plants are under construction or being designed (Table 2-4). If it is assumed that vacuum gas-oil HDS plants operate 7000 to 7500 hours a year and topped-crude HDS plants operate 6000 to 6500 hours, nearly 70 percent of the total heavy oil will be treated in 1978.

## DECOMPOSITION OF RESIDUAL OIL AND GASIFICATION DESULFURIZATION

### Flexicoking

A commercial plant with a capacity of treating 50,000 bbl/day of heavy oil by vacuum distillation and 21,000 bbl/day of residual oil from the distillator (asphalt) by Flexicoking is under construction and scheduled to be completed by the end of 1975 at Kawasaki refinery, Toa Oil. A rough material balance is shown in Figure 2-1. Vacuum gas oil from the distillator and gas oil from the Flexicoker will be treated by HDS (Gofiner). High-calorie gas will be

## Table 2-4. HYDRODESULFURIZATION PLANTS TO BE COMPLETED AFTER 1974

| Refiner | Plant site | Capacity oil, BPSD | Year of completion |
|---|---|---|---|
| Nippon Mining | Mizushima | 60,000 | 1975 |
| Asia Oil | Yokohama | 30,000[a] | 1975 |
| Asia Oil | Sakaide | 28,000[a] | 1975 |
| Toa Oil | Kawasaki | 46,000 | 1975 |
| Fuji Oil | Sodegaura | 35,000 | 1975 |
| Maruzen Oil | Chiba | 60,000[a] | 1975 |
| Idemitsu Kosan | Chiba | 34,000 | 1975 |
| Idemitsu Kosan | Tokuyama | 45,000 | 1975 |
| Idemitsu Kosan | Aichi | 50,000[a] | 1975 |
| Seibu Oil | Yamaguchi | 45,000[a] | 1975 |
| Nippon Oil | Shimomatsu | 61,000 | 1976 |
| Nippon Oil | Shimomatsu | 25,000[a] | 1976 |
| Toa Nenryo | Wakayama | 65,000[a] | 1976 |
| General Oil | Kawasaki | 40,000[a] | 1976 |
| Kashima Oil | Kashima | 40,000 | 1977 |
| Kashima Oil | Kashima | 25,000[a] | 1977 |
| Daikyo Oil | Yokkaichi | 15,000 | 1977 |
| Nippon Oil | Yokohama | 33,000[a] | 1977 |
| Koa Oil | Marifu | 30,000[a] | 1977 |
| Toa Nenryo | Shimizu | 30,000 | 1977 |
| Toa Nenryo | Shimizu | 58,000[a] | 1977 |
| Toa Nenryo | Kawasaki | 54,000[a] | 1977 |
| Mitsubishi Oil | Mizushima | 35,000 | 1977 |
| Nansei Oil | Nishihara | 55,000[a] | 1977 |
| Nippon Mining | Funakawa | 30,000 | 1978 |
| Kyushu Oil | Oita | 70,000 | 1978 |
| Fuji Kosan | Onahama | 12,000 | 1978 |
| Fuji Kosan | Onahama | 18,000[a] | 1978 |
| Nipponkai Oil | Toyama | 50,000[a] | 1978 |
| Hiuga Nenryo | Hosojima | 50,000[a] | 1978 |
| Nippon Oil | Muroran | 22,000[a] | 1978 |
| Total | | 1,251,000 | |

[a] Topped-crude HDS; other values are for vacuum gas-oil HDS.

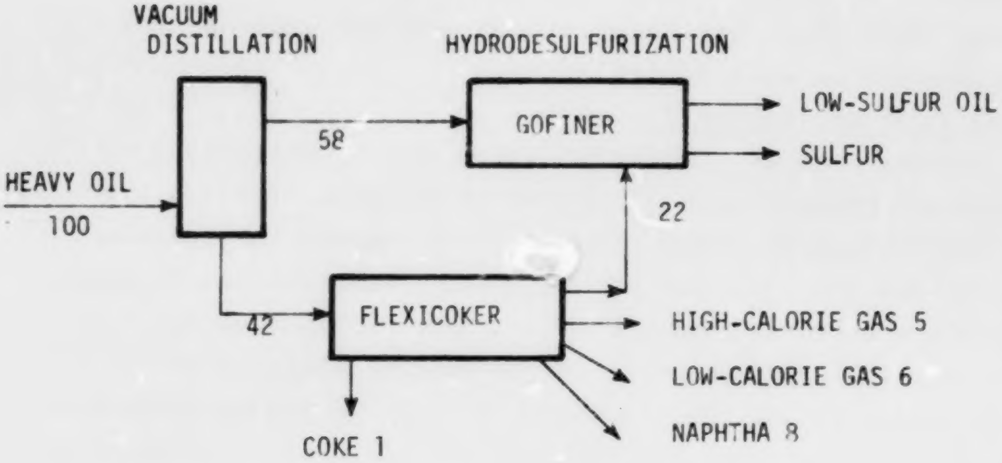

VACUUM
DISTILLATION
HYDRODESULFURIZATION
GOFINER
LOW-SULFUR OIL
SULFUR
58
HEAVY OIL
100
22
FLEXICOKER
42
HIGH-CALORIE GAS 5
LOW-CALORIE GAS 6
NAPHTHA 8
COKE 1

Figure 2-1. Material balance for residual oil decomposition by the Flexicoking process.

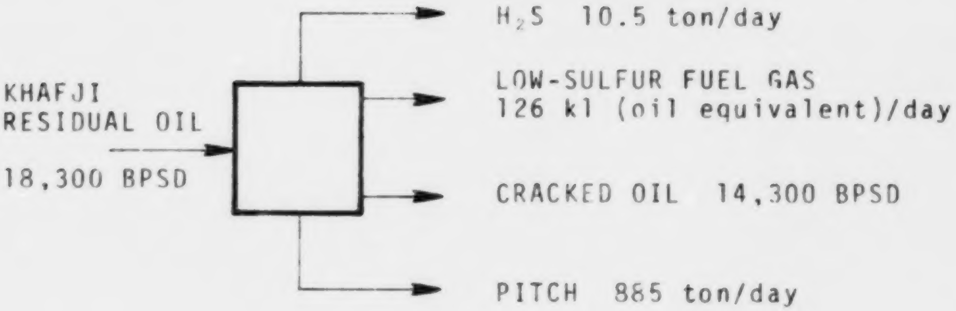

$H_2S$ 10.5 ton/day
LOW-SULFUR FUEL GAS
126 kl (oil equivalent)/day
KHAFJI
RESIDUAL OIL
18,300 BPSD
CRACKED OIL 14,300 BPSD
PITCH 885 ton/day

Figure 2-2. Material balance of the Kureha process.

sold to an adjacent steel producer, low-calorie gas will be consumed by Toa Oil, and the coke will be sold. The investment cost was estimated initially to be about $140 million (¥40 billion); negotiations are now underway for reestimation because of inflation.

Kureha Process (Eureka Process)

Kureha Chemical Industry, which has established a process of crude oil gasification to produce olefins, has recently developed a new process to decompose the residue from vacuum distillation of heavy oil (asphalt) using steam to produce a cracked oil (60-70%), gas (about 5 wt %), and pitch (25-30%)(Figure 2-2). A commercial plant owned by Eureka Industry Co. (established jointly by Kureha Chemical, Fuji Oil, Arabia Oil, and Sumitomo Metal) with a capacity of treating about a million tons of residual oil yearly is under construction at Sodegaura, Chiba prefecture, and will be completed by summer 1975.

A flowsheet of the process is shown in Figure 2-3. The residual oil containing 4 to 5 percent sulfur is maintained at 500°C for several hours in reactors. The steam serves as a heat carrier and distillation promoter. The investment cost of the commercial plant is estimated to be about $20 million (¥6 billion) within battery limits. Process requirements are as follows:

| | |
|---|---|
| Power | 3200 kW |
| Steam | 30 t/hr |
| Fuel oil | 10 kl/hr |
| Cooling water | 1000 kl/hr |
| Pure water | 44 kl/hr |
| Chemicals | $500 (¥150,000)/day |
| Operators | 4 persons per shift |

The residual oil will be supplied by Fuji Oil. The cracked oil will be sent to Fuji Oil for hydrodesulfuriza-

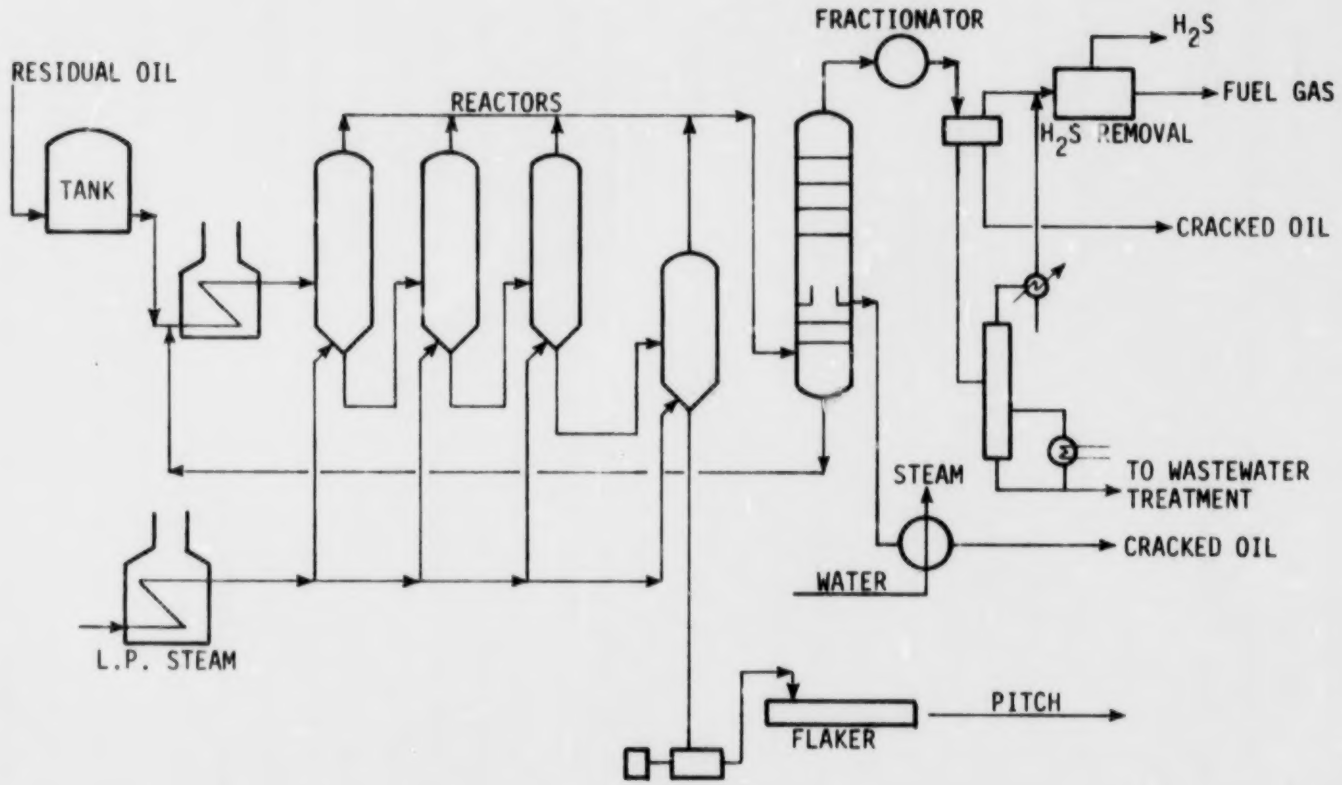

FRACTIONATOR
$H_2S$
RESIDUAL OIL
FUEL GAS
REACTORS
$H_2S$ REMOVAL
TANK
CRACKED OIL
STEAM
TO WASTEWATER TREATMENT
WATER
CRACKED OIL
L.P. STEAM
PITCH
FLAKER

Figure 2-3. Flowsheet of Kureha process.

tion. The gas from the reactor contains about 10 percent $H_2S$, which will be removed by a conventional process using an amine. The purified gas (about 16,000 kcal/$m^3$) will be used for fuel. The pitch, which contains 4 to 7 percent sulfur, will be used by Sumitomo Metal as a binder of coal for coke production. The strength of the coke is increased by the pitch.

## Ube Process

Ube Industries has been operating a prototype gasification plant with a capacity of treating 200 t/day of heavy oil. Heavy oil is gasified with oxygen and steam at 850°C under atmospheric pressure to produce high-calorie gas. Efforts have been concentrated on attaining long-term stable operation. The longest continuous operation period attained so far is nearly one month. Low-sulfur heavy oil has been used because desulfurization facilities have not been installed yet. An IFP reactor will be installed for the desulfurization after more stable operation is reached.

## Coal Gasification

The Coal Research Center has recently resumed tests on coal gasification. Pilot plants with capacities of treating 5 tons and 40 tons will be completed by January 1975 and by the end of 1976, respectively, in Yubari, Hokkaido. Coal will be gasified in a fluidized bed under 10 atmospheres pressure at 800 to 900°C with air and steam to produce a low-calorie gas (1200 to 1500 cal/$m^3$). A wet process will be used for desulfurization of the gas. The Coal Research Center has developed a fluidized drying process for coals which has been used commercially.

Electric Power Development Co., which has used coal for utility boilers, is considering introducing coal gasification technology from abroad. Because the Lurgi process seems unsuitable to Japanese coal, which has a slagging tendency, processes being developed in the United States are under consideration.

## STATUS OF FLUE GAS DESULFURIZATION

Table 2-5 shows major $SO_2$ removal processes, numbers of plants, and the total capacities (amounts of gas treated). The Table includes plants in operation and under construction and those ordered before October 1974. Most of the plants ordered will be completed by the end of 1976. The sum of the capacities is 60 million $Nm^3$/hr, which is equivalent to 20,000 MW. About half of the gas is from utility boilers; the rest is from industrial boilers and other sources, such as sulfuric acid and iron ore sintering plants. The wet lime-limestone Mitsubishi-JECCO process is most widely used, treating more than one-fourth of the total gas in Japan.

A salient feature of the desulfurization efforts in Japan is that they are oriented toward processes that yield salable by-products. This is because Japan is subject to limitations in domestic supply of sulfur and its compounds as well as in land space available for disposal of useless by-products. About 65 percent of the $SO_2$ recovered at the plants listed in Table 2-5 is converted into salable gypsum, 15 percent into sodium sulfite, 15 percent into sulfuric acid, and the rest into waste calcium sulfite and sodium and ammonium sulfates. Because use of desulfurization is increasing rapidly, the supply of by-products may soon exceed the demand.

Two processes for removal of $H_2S$ from coke-oven gas and other gases have been recently developed and are widely used in Japan. One is the Takahax process developed by Kinon Chemicals, which uses an alkaline solution containing a catalyst (1, 4-naphthoquinone-2-sulfonic acid) as the absorbent. The other is the Fumaks process developed by Osaka Gas Co. jointly with Sumitomo Chemical Engineering Co. using an alkaline solution containing 0.1 percent catalyst (picric acid) as the absorbent. The total capacity has exceeded 2 million $Nm^3$/hr. Both processes by-produce elemental sulfur.

Table 2-5. $SO_2$ RECOVERY PROCESSES AND PLANT CAPACITIES

| Process | Absorbent | By-product | Number of plants | Total capacity, $10^3$ $Nm^3/hr$ |
|---|---|---|---|---|
| Mitsubishi-JECCO | $CaO$, $CaCO_3$ | Gypsum | 31 | 17,908 |
| Kureha-Kawasaki | $Na_2SO_3$-$CaCO_3$ | Gypsum | 6 | 5,925 |
| Wellman-MKK | $Na_2SO_3$ | $H_2SO_4$ | 11 | 5,320 |
| Chiyoda | $H_2SO_4$-$CaCO_2$ | Gypsum | 13 | 4,341 |
| Oji | NaOH | $Na_2SO_3$ | 49 | 3,839 |
| Babcock-Hitachi | $CaCO_3$ | Gypsum | 5 | 3,191 |
| IHI-TCA | NaOH | $Na_2SO_3$ | 26 | 2,787 |
| Mitsui Miike | $CaCO_3$ | Gypsum | 5 | 2,739 |
| Tsukishima-Bahco | NaOH | $Na_2SO_3$ | 20 | 2,655 |
| Kurabo | NaOH | $Na_2SO_3$ | 70 | 2,580 |
| Showa Denko-Ebara | $Na_2SO_3$-$CaCO_3$ | Gypsum | 16 | 2,458 |
| Chemico-IHI | $CaCO_3$ | Gypsum | 2 | 1,800 |
| Kureha | NaOH | $Na_2SO_3$ | 8 | 1,431 |
| Wellman-SCEC | $Na_2SO_3$ | $H_2SO_4$ | 6 | 1,298 |
| Nippon Kokan | $NH_3$ | $(NH_4)_2SO_4$ | 1 | 760 |
| Tsukishima | $Na_2SO_3$-CaO | Gypsum | 4 | 714 |
| MKK | NaOH | $Na_2SO_4$ | 17 | 693 |
| Fuji Kasui | CaO, $CaCO_3$ | Gypsum | 7 | 682 |
| Chemico-Mitsui | MgO | $SO_2$ S | 1 | 500 |
| Hitachi-Tokyo E.P. | C-$CaCO_3$ | Gypsum | 1 | 420 |
| Chemico-Mitsui | $Ca(OH)_2$ | $CaSO_3$ | 1 | 385 |
| Showa Denko | NaOH | $Na_2SO_3$ | 2 | 370 |
| Chubu-MKK | $CaCO_3$ | Gypsum | 2 | 311 |
| Kurabo | $(NH_4)_2SO_4$-CaO | Gypsum | 4 | 303 |
| Dowa | $Al_2(SO_4)_3$-$CaCO_3$ | Gypsum | 2 | 280 |
| Nippon Kokan | CaO | Gypsum | 2 | 227 |
| Nippon Kokan | $(NH_4)_2SO_3$-CaO | Gypsum | 1 | 150 |

# 3. WET LIME-LIMESTONE PROCESSES FOR $SO_2$ RECOVERY

## INTRODUCTION

$SO_2$ removal plants using wet lime-limestone processes with capacities larger than 20 MW equivalent are listed in Table 3-1. The Mitsubishi-JECCO process has been used most widely for oil-fired boilers, iron-ore sintering plants, etc., whereas the Chemico-Mitsui and Mitsui Miike processes have been applied to coal-fired boilers. Five other processes have also been used, mainly for flue gas from oil-fired boilers. Many of the plants use lime to obtain a high $SO_2$ removal efficiency--more than 90 percent--which is required in many districts in Japan. Limestone scrubbing removes 85 to 90 percent of the $SO_2$ at 0.9 to 1.2 stoichiometry with a scrubber nearly twice as tall as that used with lime.

A schematic flowsheet is shown in Figure 3-1; this flow is common to most processes except the Chemico-Mitsui and Mitsui Miike processes, which do not use coolers (prescrubbers). The flue gas is passed from an electrostatic precipitator through a cooler, scrubber, mist eliminator, and reheater and led into a stack. Types of scrubbers and examples of operation parameters are listed in Table 3-2. Calcium sulfite formed by the reaction of $SO_2$ with lime or limestone slurry is oxidized by air bubbling into gypsum, which is then centrifuged. Major components and characteristics of the process are described in the following paragraphs.

Table 3-1. MAJOR SULFUR DIOXIDE SCRUBBING INSTALLATIONS IN JAPAN

(LIME-LIMESTONE SCRUBBING)

| Process developer | User | Plant site | Absorbent | MW[a] | Type of plant[b] | Year of completion | Gypsum, tons/day |
|---|---|---|---|---|---|---|---|
| Mitsubishi-JECCO | Kansai Electric | Amagasaki | $Ca(OH)_2$ | 30 | Utility boiler | 1972 | 20 |
| Mitsubishi-JECCO | Ohahama Smelter | Onahama | $Ca(OH)_2$ | 29 | Copper smelter | 1972 | 400 |
| Mitsubishi-JECCO | Kawasaki Steel | Chiba | $Ca(OH)_2$ | 37 | Sintering plant | 1973 | 15 |
| Mitsubishi-JECCO | Kansai Electric | Kainan | $Ca(OH)_2$ | 150 | Utility boiler | 1974 | 20 |
| Mitsubishi-JECCO | Tohoku Electric | Hachinoe | $Ca(OH)_2$ | 125 | Utility boiler | 1974 | 50 |
| Mitsubishi-JECCO | Tokyo Electric | Yokosuka | $CaCO_3$ | 130 | Utility boiler | 1974 | 20 |
| Mitsubishi-JECCO | Kyushu Electric | Karita | $Ca(OH)_2$ | 175 | Utility boiler | 1974 | 70 |
| Mitsubishi-JECCO | Kawasaki Steel | Mizushima | $Ca(OH)_2$ | 232 | Sintering plant | 1974 | 120 |
| Mitsubishi-JECCO | Kawasaki Steel | Mizushima | $Ca(OH)_2$ | 279 | Sintering plant | 1975 | 90 |
| Mitsubishi-JECCO | Kawasaki Steel | Chiba | $Ca(OH)_2$ | 130 | Sintering plant | 1975 | 27 |
| Mitsubishi-JECCO | Kansai Electric | Amagasaki | $Ca(OH)_2$ | 125 | Sintering plant | 1975 | 40 |
| Mitsubishi-JECCO | Teijin | Ehime | $Ca(OH)_2$ | 83 | Industrial boiler | 1975 | 85 |
| Mitsubishi-JECCO | Mizushima Power | Mizushima | $Ca(OH)_2$ | 192 | Utility boiler | 1975 | 95 |
| Mitsubishi-JECCO | Niigata Power | Niigata | $CaCO_3$ | 117 | Utility boiler | 1975 | 43 |
| Mitsubishi-JECCO | Kyushu Electric | Katsura | $CaCO_3$ | 250 | Utility boiler | 1975 | 70 |
| Mitsubishi-JECCO | Kyushu Electric | Katsura | $CaCO_3$ | 175 | Utility boiler | 1976 | 45 |
| Mitsubishi-JECCO | Kyushu Electric | Ainoura | $CaCO_3$ | 250 | Utility boiler | 1976 | 95 |
| Mitsubishi-JECCO | Kyushu Electric | Ainoura | $CaCO_3$ | 250 | Utility boiler | 1976 | 95 |
| Mitsubishi-JECCO | Chugoku Electric | Owase | $Ca(OH)_2$ | 375 | Utility boiler | 1976 | 330 |
| Mitsubishi-JECCO | Chugoku Electric | Owase | $Ca(OH)_2$ | 375 | Utility boiler | 1976 | 330 |
| Chemico-Mitsui | Mitsui Aluminum | Omuta | $Ca(OH)_2$ | 119[c] | Industril boiler | 1972 | [d] |
| Mitsui Miike | Mitsui Aluminum | Omuta | $CaCO_3$ | 25[c] | Industrial boiler | 1974 | 20 |
| Mitsui Miike | Mitsui Aluminum | Omuta | $CaCO_3$ | 175[c] | Industrial boiler | 1975 | 200 |
| Mitsui Miike | Elec. Pow. Dev. | Takasago | $CaCO_3$ | 250[c] | Utility boiler | 1974 | 200 |
| Bahco-Tsukishima | Yahagi Iron | Nagoya | $Ca(OH)_2$ | 26 | Sintering plant | 1971 | 25 |
| Babcock-Hitachi | Chugoku Electric | Mizushima | $CaCO_3$ | 104 | Utility boiler | 1974 | 25 |
| Babcock-Hitachi | Chugoku Electric | Tamashima | $CaCO_3$ | 500 | Utility boiler | 1975 | 350 |
| Ishikawajima-TCA | Chichibu Cement | Kumagaya | $Ca(OH)_2$ | 62 | Diesel engine | 1972 | 22 |
| Sumitoma-Fuji Kasui | Sumitomo Metal | Kokura | $Ca(OH)_2$ | 32 | Heating furnace | 1974 | 25 |
| Chubu-MKK | Ishihara Sangyo | Yokkaichi | $CaCO_3$ | 77 | Industrial boiler | 1974 | 50 |
| Chubu-MKK | Mitsubishi Gas | Yokkaichi | $Ca(OH)_2$ | 22 | Industrial boiler | 1974 | 12 |

[a] Actual for boilers and equivalent gas flow for others (at 3,100 $Nm^3$/hr per MW).

[b] Boilers are oil-fired unless otherwise noted.

[c] Coal-fired.

[d] Waste sludge of calcium sulfite.

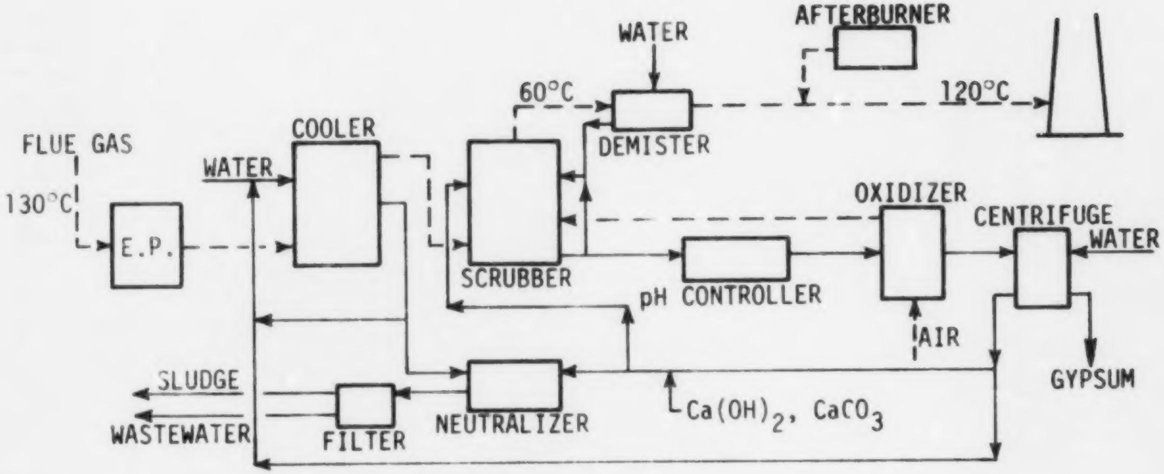

FLUE GAS
130°C
E.P.
WATER
COOLER
60°C
SCRUBBER
WATER
DEMISTER
AFTERBURNER
120°C
pH CONTROLLER
OXIDIZER
AIR
CENTRIFUGE
WATER
GYPSUM
SLUDGE
WASTEWATER
FILTER
NEUTRALIZER
Ca(OH)2, CaCO3

Figure 3-1. Schematic flowsheet of wet lime/limestone process.

## Table 3-2. EXAMPLE OF OPERATION PARAMETERS OF FGD PLANTS BY-PRODUCING GYPSUM AND CALCIUM SULFITE

| Process developer | Absorbent, precipitant (stoichiometry) | Capacity, $10^3$ $Nm^3$/hr | Type of absorber | Slurry or solution pH | Slurry or solution conc., % | L/G, liters/$Nm^3$ | Gas velocity, m/sec | Pressure drop[a] mm $H_2O$ | $SO_2$ in, ppm | $SO_2$ out, ppm | Moisture in gypsum, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wet lime-limestone process | | | | | | | | | | | |
| Mitsubishi-JECCO | $Ca(OH)_2$ 0.9-1 | 550 | GP[b] | 6-7 | 15 | 6-7 | 3 | 150 | 800 | 75 | 8-10 |
| Mitsubishi-JECCO | $CaCO_3$ 0.9-1 | 400 | GP | 5-6 | 12 | 7-8 | 3 | 120 | 250 | 30 | 7-8 |
| Chemico-Mitsui | $Ca(OH)_2$ 1-1.05 | 385 | Venturi | 7 | 3-5 | 10-15 | | 400 | 2,000 | 200 | $CaSO_3$ |
| Mitsui Miike | $CaCO_3$ 0.9-1 | 70 | Venturi | 6 | 5 | 10-15 | | | 2,000 | 200 | 10-15 |
| Babcock-Hitachi | $CaCO_3$ 1-1.2 | 320 | PP[c] | 6.2 | 7-8 | 7 | 4 | 500 | 400 | 40 | 7-8 |
| Chubu-MKK | $CaCO_3$ | 250 | Screen | 6 | 10 | 10 | 4 | 80 | 1,500 | 200 | 10-12 |
| Ishikawajima | $Ca(OH)_2$ | 100 | TCA | | 2 | 7 | 3 | | 700 | 50 | 10-15 |
| Sumitomo-Fuji Kasui | $Ca(OH)_2$ 1-1.2 | 60 | PP[c] | 6 | 10 | 10 | 4 | 450 | 1,000 | 50 | 10-12 |
| Indirect lime-limestone process | | | | | | | | | | | |
| Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | 400 | GP[b] | 7 | 20 | 1-2 | | 200 | 800 | 20 | 6-7 |
| Showa Denko | $Na_2SO_3$, $CaCO_3$ | 500 | Cone[d] | 6.8 | 25 | 1-2 | | | 1,400 | 40 | 8-10 |
| Nippon Kokan | $(NH_4)_2SO_3$, $Ca(OH)_2$ | 150 | Screen | 6 | 30 | 2 | 3 | 250 | 700 | 30 | 8-10 |
| Chiyoda | dil.$H_2SO_4$, $CaCO_3$ | 750 | Tellerette | 1 | 2-4 | 30-45 | 1 | | 600 | 50 | 7-9 |
| Kurabo | $(NH_4)_2SO_4$, $Ca(OH)_2$ | 5 | Tellerette | 3-4 | 10 | 6-10 | 2 | 50 | 1,500 | 80 | 9-10 |
| Dowa | $Al_2(SO_4)_3$, $CaCO_3$ | 140 | Tellerette | 3-4 | 10 | 3-9 | 1.5 | 100 | 600 | 20 | 10-12 |
| Hitachi-Tokyo Elec. | Carbon, $CaCO_3$ | 420 | Packed[e] | | | | 0.5 | 480 | 500 | 80 | 9-11 |

[a] Pressure drop includes that of absorber and mist eliminator.

[b] Grid packed.

[c] Perforated plate.

[d] Four scrubbers.

[e] Six towers.

## Cooler

Flue gas first enters the cooler (prescrubber), where the gas is sprayed with water. The cooler, which is not commonly used in the United States, has three functions: (1) cooling and humidifying the gas to aid in prevention of scaling in the scrubber; (2) protecting coatings and packings made of plastic; (3) removing dust and other impurities in the gas that were not caught by the electrostatic precipitator. This is useful in obtaining high purity by-products with good commercial value. Because impurities in the gas, such as dust and chloride, accumulate in the liquor, a portion of the liquor is sent to the water treatment system, neutralized to precipitate heavy metals, filtered, and then usually purged.

## Scrubber

Scrubber design varies among the processes. The scrubber is a plastic grid packed tower for Mitsubishi-JECCO, a venturi for Chemico-Mitsui and Mitsui Miike, a TCA with polyethylene balls for Ishikawajima, a Bahco type for Tsukishima, a stainless steel screen type for Chubu-Mitsubishi Chubu-MKK (CM), and perforated plates for Babcock-Hitachi and Sumitomo-Fuji Kasui processes. The reliability of the Mitsubishi-JECCO and Chemico scrubbers has been well demonstrated in Japan. The former has less pressure drop. The TCA scrubber has a high $SO_2$ removal efficiency but presents the problem of wearing of balls. The Bahco and screen type scrubbers might be more susceptible to scaling. The perforated plate scrubber for the Sumitomo-Fuji Kasui process (Moretana type) is designed to give extreme turbulence producing foam layers 15 to 20 inches thick; a high $SO_2$ removal efficiency is attained while heavy mist is formed.

For the Chemico-Mitsui and Mitsui Miike processes, which use no cooler, the scrubber is operated with a dilute slurry at a high L/G ratio to prevent scaling. The by-product contains a considerable amount of impurities, as described in Section 6.

### Oxidation

The rotary atomizer invented by JECCO has been used for the Mitsubishi-JECCO, Babcock-Hitachi, and Chubu-MKK processes because of its high efficiency and reliability. Different types of oxidizers have been developed for other processes. A low pH (3.5 to 4.0) is desirable for oxidation of calcium sulfite slurry. This is attained with a pH controller by adding a small amount of sulfuric acid, as is being done at many plants, or by using flue gas and a catalyst, as in the Mitsui Miike process. The facilities to produce gypsum, pH controller, oxidizer and centrifuge account for about 30 percent of the total investment cost. Nevertheless, production of gypsum has been growing in Japan. Mitsui Aluminum Co. which has been producing waste calcium sulfite sludge will change the process to by-produce gypsum, as described later. By-production of calcium sulfite sludge and its stabilization, as it is being done in the United States, might be of much interest in the future in Japan when there is an oversupply of gypsum.

### Saturated- or Unsaturated-Mode Operation

Scaling has been the largest problem for the wet lime-limestone process. It is known that the formation of gypsum crystals tends to cause the scaling. A theory of unsaturated-mode operation (operation without the presence of gypsum) has been developed recently in the United States[2] and applied successfully to the operation of Paddy's Run Station, Louisville Gas and Electric Company. The theory is based on the fact that when the degree of oxidation of calcium sulfite is below 20 percent, sulfate ions could be contained in calcium sulfite crystals replacing sulfite ions and thus preventing the formation of gypsum crystals. The author's X-ray diffraction study of sludge obtained from Omuta plant, Mitsui Aluminum Co., supports the theory, as discussed later.

In most plants in Japan, the $O_2/SO_2$ ratio of flue gas is high and oxidation in the scrubber exceeds 20 percent, resulting in the formation of gypsum crystals. In order to ensure scaling-free operation in such a saturated mode, improvements have been made in the design, fabrication, and operation of the plants. Use of good quality seed of gypsum crystals is an important key to the prevention of scaling. Scaling tends to occur most readily on mist eliminators. In many plants, mist eliminators are washed with fresh water to prevent scaling, but this procedure increases the amount of wastewater. In some plants - for example, Kainan plant of Kansai Electric operating by the Mitsubishi-JECCO process - the mist eliminator is washed with a supernatant of calcium sulfite-gypsum slurry in some improved way without any scale formation.

## Water Balance

Fresh water, about 1 ton per 10 MW, is fed into the cooler to lower the flue gas temperature from a range of 130 to 140°C to a range of 55 to 60°C. Most of the water is volatilized or recycled and a portion is usually purged after being treated. In most plants, the mist eliminator and by-product gypsum are washed with fresh water. The amount of the input water usually exceeds the output, i.e. water is taken into gypsum as water of crystallization and moisture. (Moisture content of gypsum after being centrifuged is normally about 10 percent.) Therefore, a portion of the liquor discharged from the gypsum centrifuge is also sent to the wastewater treatment system and then purged. In Japan it is allowable to purge water after treating it to meet the regulations on pH, heavy metals, COD, etc.

To minimize the use of fresh water and the emission of wastewater, some plants feed the water discharged from the cooler into the scrubbing system, wash the mist eliminator with a supernatant of the calcium sulfite-gypsum slurry, and omit the water wash of the product gypsum. Still some water is purged from the system to prevent the accumulation of chloride and other impurities, because chloride promotes corrosion and also impairs the quality of gypsum for use in wallboard.

The amounts of wastewater and of by-product gypsum at five plants are shown in Table 3-3. For the three plants using the Mitsubishi-JECCO process, the water ratio (A+C)/(A+B+C) ranges from 0.37 to 0.64 and is lower with the higher concentration of $SO_2$ in flue gas. In plants using other processes, the ratios are higher.

In the United States, calcium sulfite sludge containing about 50 percent moisture is discarded while the supernatant and filtrate are recycled without releasing any water. This system is called "closed loop" operation, although the water ratio is about 0.5. Compared with the closed loop, the actual amount of water removed is about equal for the Karita plant and less for the Owase plant using the Mitsubishi-JECCO process.

## MITSUBISHI-JECCO LIME-LIMESTONE PROCESS

### State of Development

Mitsubishi Heavy Industries (MHI) constructed the first wet-lime process plant in 1964, licensed by Japan Engineering Consulting Co. (JECCO). The plant is located at Koyasu Fertilizer Works, Nippon Kokan, and treats a tail gas from a sulfuric acid plant emitted at a rate of 62,500 $Nm^3/hr$ and containing 2200 ppm $SO_2$. Although several problems, including scaling and corrosion, were encountered at the beginning of the operation, these have been solved by the cooperation of MHI and Nippon Kokan. Recently MHI constructed several

Table 3-3. AMOUNTS OF WASTEWATER AND GYPSUM

| Process | User | Plant site | MW | $SO_2$, ppm | Waste-water, t/hr (A) | Gypsum, t/hr | | Water ratio (A+C)/(A+B+C) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Solid (B) | Water (C) | |
| Mitsubishi-JECCO | Kansai Electric | Kainan | 150 | 270 | 1.5 | 0.9 | 0.1 | 0.64 |
| Mitsubishi-JECCO | Kyushu Electric | Karita | 175 | 800 | 2.9 | 2.9 | 0.3 | 0.52 |
| Mitsubishi-JECCO | Chubu Electric | Owase[a] | 750 | 1,480 | 14.0 | 29.0 | 2.9 | 0.37 |
| Babcock-Hitachi | Chugoku Electric | Mizushima | 105 | 400 | 4.0 | 0.9 | 0.1 | 0.82 |
| Chubu-MKK | Ishihara Chem. | Yokkaichi | 85 | 1,300 | 4.0 | 2.2 | 0.2 | 0.67 |

[a] Designed value; the plant is under construction.

plants, which are operating satisfactorily. Many new plants are under construction, as shown in Table 3-4.

Process Description

Figure 3-2 shows a flowsheet of a lime-process plant at Amagasaki Station, Kansai Electric, with a capacity of treating 100,000 $Nm^3$/hr of flue gas from oil-fired boilers. Waste gas is first washed with water to remove dust and to cool the gas to about 60°C. As the water becomes acidic and dissolves metallic components of dust, it is neutralized with milk of lime to precipitate metallic ions, which are filtered off with the dust. The filtrate is used for slaking of lime. The cooled gas is then sent to an absorbing step. Two plastic-grid packed absorbers in series are housed in one tower. Milk of lime is fed to the No. 2 absorber. The gas is introduced into the No. 1 absorber and then into the No. 2 absorber. The slurry discharged from the No. 2 absorber is a mixture of calcium sulfite and unreacted lime with a small amount of gypsum. The slurry is then led to the No. 1 absorber, where the remaining lime is reacted to form calcium sulfite, and a portion of the sulfite is converted to bisulfite. The pH of the slurry discharged from the No. 1 absorber is 4 to 4.5. The concentration of the slurries in the absorbers is about 15 percent. A relatively high liquid/gas ratio (6 to 7 liters/$Nm^3$) is used to prevent scaling.

The pH of the slurry is then adjusted to 3.5 to 4 to promote oxidation in the following step. If required, a small amount of sulfuric acid, normally less than 1 ton per 100 tons of inlet $SO_2$, is added to the slurry for the adjustment. The slurry is then sent to an oxidizing tower where the sulfite and bisulfite are converted to gypsum by air oxidation using rotary atomizers (invented by JECCO) at a pressure of 4 to 5 atmospheres (44 to 58 psig) and a temperature of 60 to 80°C. The atomizer is effective in producing fine bubbles and is free from scaling, erosion, and corrosion. The gas leaving the oxidizer contains some

Table 3-4. WET LIME-LIMESTONE PROCESS PLANTS USING THE MITSUBISHI-JECCO PROCESS

| No. | User | Plant site | Capacity, Nm$^3$/hr[a] | Source of gas | $SO_2$, ppm |  | Absorbent | Year of completion |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | inlet | outlet |  |  |
| 1 | Nippon Kokan | Koyasu | 62,500 | $H_2SO_4$ plant | 2,200 | 200 | $Ca(OH)_2$ | 1964 |
| 2 | Kansai Electric | Amagasaki | 100,000 | Utility boiler | 700 | 70 | $Ca(OH)_2$ | 1972 |
| 3 | Onahama Refining | Onahama | 92,000 | Copper smelter | 20,000 | 100 | $Ca(OH)_2$ | 1972 |
| 4 | Kawasaki Steel | Chiba | 120,000 | Sintering plant | 600 | 60 | $Ca(OH)_2$ | 1973 |
| 5 | Yoshino Gypsum | Tokyo | 12,000 | Industrial boiler | 1,400 | 130 | $Ca(OH)_2$ | 1973 |
| 6 | Kansai Electric | Kainan | 400,000 | Utility boiler | 550 | 60 | $Ca(OH)_2$ | 1974 |
| 7 | Tokyo Electric | Yokosuka | 400,000 | Utility boiler | 250 | 40 | $CaCO_3$ | 1974 |
| 8 | Tohoku Electric | Hachinohe | 380,000 | Utility boiler | 850 | 85 | $Ca(OH)_2$ | 1974 |
| 9 | Kyushu Electric | Karita | 550,000 | Utility boiler | 800 | 75 | $Ca(OH)_2$ | 1974 |
| 10 | Kawasaki Steel | Mizushima | 750,000 | Sintering plant | 830 | 40 | $Ca(OH)_2$ | 1974 |
| 11 | Kansai Electric | Amagasaki | 375,000 | Utility boiler | 500 | 50 | $Ca(OH)_2$ | 1975 |
| 12 | Niigata Power | Niigata | 530,000 | Utility boiler | 700 | 70 | $CaCO_3$ | 1975 |
| 13 | Kawasaki Steel | Mizushima | 900,000 | Sintering plant | 500 | 40 | $Ca(OH)_2$ | 1975 |
| 14 | Kawasaki Steel | Chiba | 320,000 | Sintering plant | 800 | 64 | $Ca(OH)_2$ | 1975 |
| 15 | Teijin | Ehime | 270,000 | Industrial boiler | 1,700 | 60 | $Ca(OH)_2$ | 1975 |
| 16 | Mizushima Power | Mizushima | 611,600 | Utility boiler | 1,050 | 40 | $Ca(OH)_2$ | 1975 |
| 17 | Tohoku Electric | Niigata | 420,000 | Utility boiler | 550 | 55 | $CaCO_3$ | 1976 |
| 18 | Chubu Electric | Owase | 1,200,000 | Utility boiler | 1,500 | 35 | $Ca(OH)_2$ | 1976 |
| 19 | Chubu Electric | Owase | 1,200,000 | Utility boiler | 1,500 | 35 | $Ca(OH)_2$ | 1976 |
| 20 | Kawasaki Steel | Mizushima | 750,000 | Sintering plant | 550 | 40 | $Ca(OH)_2$ | 1976 |
| 21 | Toyobo | Iwakuni | 200,000 | Industrial boiler | 1,400 | 50 | $Ca(OH)_2$ | 1976 |
| 22 | Kashima Power | Kashima | 431,000 | Utility boiler | 1,000 | 100 | $CaCO_3$ | 1976 |
| 23 | Kyushu Electric | Karatsu | 730,000 | Utility boiler | 550 | 70 | $CaCO_3$ | 1976 |
| 24 | Kyushu Electric | Karatsu | 570,000 | Utility boiler | 550 | 70 | $CaCO_3$ | 1976 |
| 25 | Kyushu Electric | Ainoura | 730,000 | Utility boiler | 880 | 110 | $CaCO_3$ | 1976 |
| 26 | Kyushu Electric | Ainoura | 730,000 | Utility boiler | 880 | 110 | $CaCO_3$ | 1976 |
| 27 | Confidential |  | 1,100,000 | Utility boiler | 950 | 50 | $CaCO_3$ | 1976 |
| 28 | Confidential |  | 1,100,000 | Utility boiler | 950 | 50 | $CaCO_3$ | 1976 |
| 29 | Confidential |  | 1,200,000 | Utility boiler | 1,600 | 50 | $CaCO_3$ | 1976 |
| 30 | Confidential |  | 475,000 | Utility boiler | 500 | 65 | $Ca(OH)_2$ | 1976 |
| 31 | Confidential |  | 1,200,000 | Utility boiler | 550 | 65 | $Ca(OH)_2$ | 1976 |

[a] 1000 Nm$^3$/hr = 590 scfm = 320 kW.

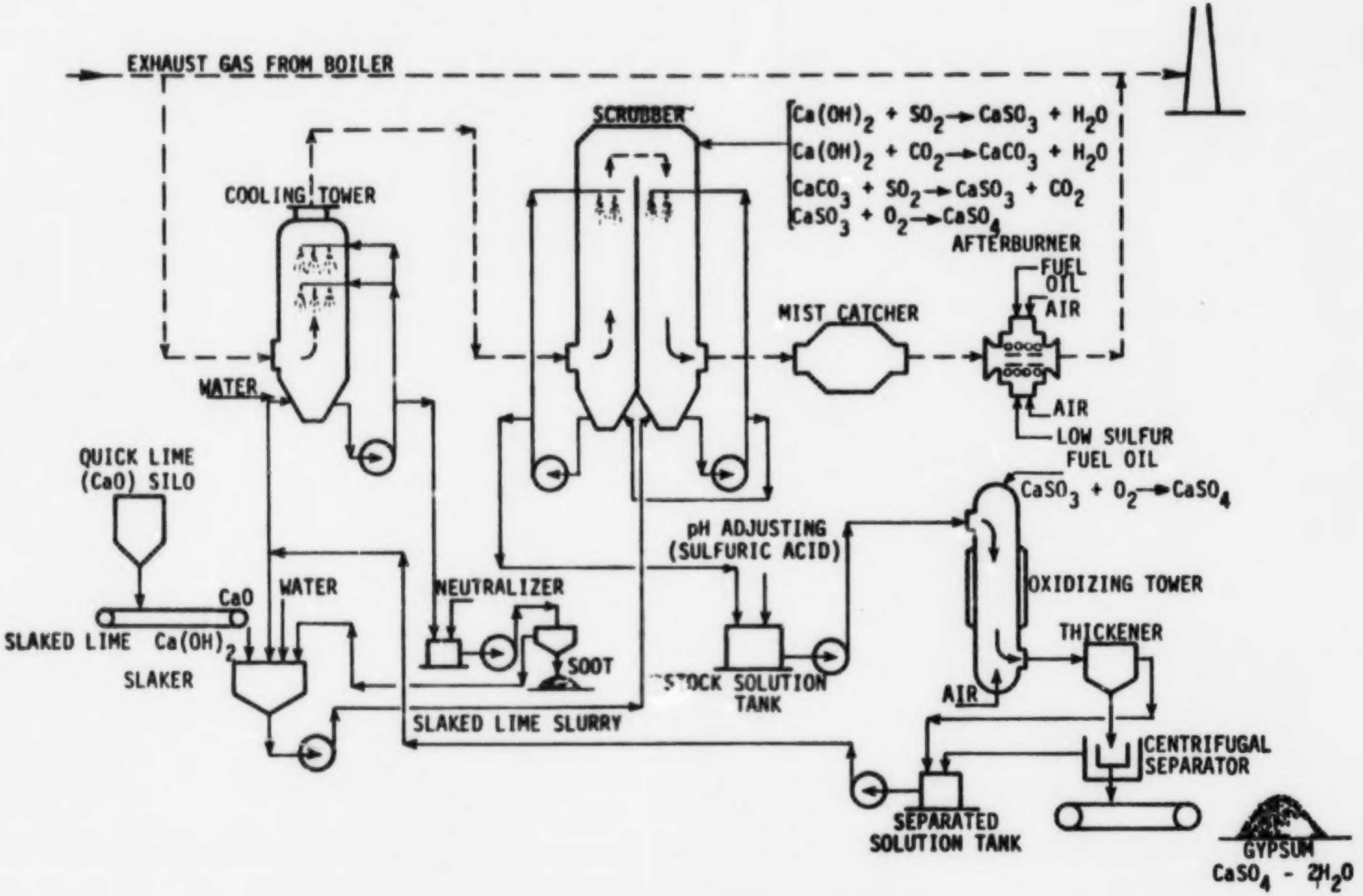

EXHAUST GAS FROM BOILER
COOLING TOWER
SCRUBBER
$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$
$CaSO_3 + O_2 \rightarrow CaSO_4$
AFTERBURNER
FUEL OIL
AIR
MIST CATCHER
AIR
LOW SULFUR FUEL OIL
WATER
QUICK LIME (CaO) SILO
$CaSO_3 + O_2 \rightarrow CaSO_4$
pH ADJUSTING (SULFURIC ACID)
OXIDIZING TOWER
CaO
WATER
NEUTRALIZER
SLAKED LIME $Ca(OH)_2$
SLAKER
SOOT
STOCK SOLUTION TANK
THICKENER
AIR
SLAKED LIME SLURRY
CENTRIFUGAL SEPARATOR
SEPARATED SOLUTION TANK
GYPSUM
$CaSO_4 - 2H_2O$

Figure 3-2. Flowsheet of Mitsubishi-JECCO lime/limestone process (Amagasaki plant, Kansai Electric) (Two-tower system).

$SO_2$, and is returned to the absorber. The gypsum is centrifuged. All of the liquor is returned to the system. The gypsum grows into large crystals; moisture content after centrifugation is only 8 to 10 percent. The gypsum thus obtained is of high purity and good quality, suitable for use in cement and gypsum board. The gas from the No. 2 absorber is passed through a demister, reheated, and led to a stack. More than 90 percent of the $SO_2$ is recovered.

For most of the later plants, a single-absorber system, as shown in Figure 3-3, is used to reduce the plant cost. Plant No. 29 (in Table 3-4) will use a double-absorber system to remove 97 percent of the $SO_2$ (1600 ppm) with limestone. For the single-absorber system, a cooling tower and an absorbing tower are put together. Flue gas goes up the cooler and down the absorber. In this system, the pH of the outlet slurry discharged from the absorber tends to be higher than that in the double-absorber system. Consequently, a considerable amount of sulfuric acid, 5 to 10 tons per 100 tons of inlet $SO_2$, is normally required for pH adjusting prior to the oxidation step.

### Status of Technology

By means of extensive studies with a pilot plant, Mitsubishi has determined that scaling can be prevented by shape and arrangement of the grid in the absorber; by adjustment of the slurry concentration, pH, and liquid/gas ratio; and by addition of gypsum crystal seed and by thorough mixing of the lime in the circulating slurry.

The Amagasaki plant has been in continuous operation for most of the time since operation began in April 1972, except for the period of shutdown of the power plant. The desulfurization plant treats a flue gas containing about 700 ppm $SO_2$ to recover about 90 percent of the $SO_2$. This plant was operated with a closed loop, emitting no water at all, for 3 months after start-up. But, as chloride and other

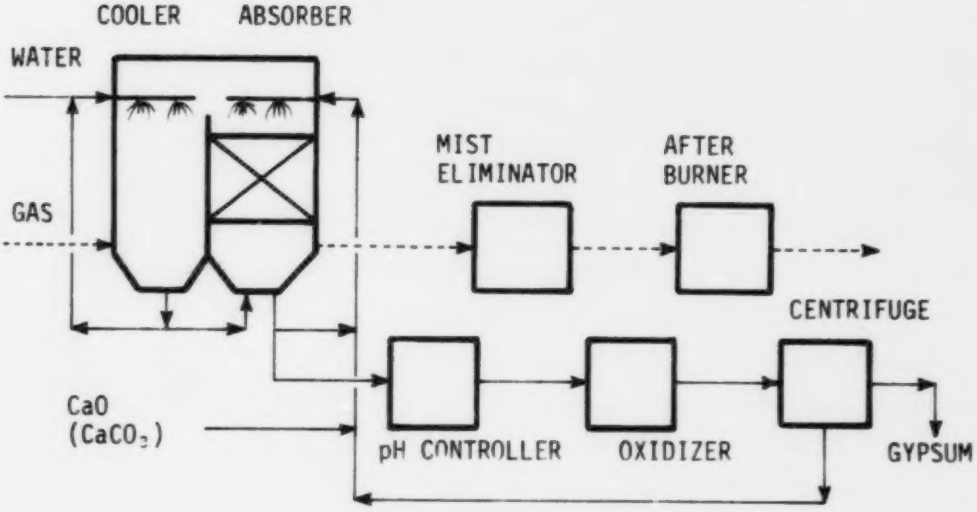

COOLER
ABSORBER
WATER
GAS
MIST ELIMINATOR
AFTER BURNER
CENTRIFUGE
CaO
(CaCO3)
pH CONTROLLER
OXIDIZER
GYPSUM

Figure 3-3. Single-tower system (Mitsubishi-JECCO process).

impurities derived from fuel, lime, and water accumulated in the circulating liquor, symptoms of corrosion of the structural material appeared and quality of the by-product gypsum decreased. Since then a small amount of water has been removed from the system to maintain the impurities under a certain level. The Onahama plant (No. 3 in Table 3-4; Figure 3-4), which treats a waste gas from a copper smelter (92,000 $Nm^3/hr$, $SO_2$-20,000 ppm), had some scaling problem at the beginning. Because a large amount of lime slurry was fed from the top of the second scrubber to absorb more than 99 percent of the $SO_2$ of very high concentration, the pH of the slurry at the upper part of the scrubber was too high and the slurry absorbed $CO_2$ to form $CaCO_3$, which caused the scaling. Some modification was made to charge the lime slurry into several places and thus the problem was solved. High-pressure washing for about 3 hours once every month or so is adequate, since the deposits tend to be soft. The plant has been producing 400 tons of gypsum per day, all of which has been used for wallboard by Onahama-Yoshino Co., a company established for wallboard production using the by-product. Operation of other plants (Nos. 4 - 10 in Table 3-4) has been good since start-up, except for the Hachinohe plant, Tohoku Electric, which experienced mechanical troubles, due partly to misoperation, that required more than 2 months to resolve. Yoshino Gypsum has been producing calcium sulfite (without oxidizer) and has been using the sulfite for a special purpose. Operational data for the Kainan plant, Kansai Electric (Figure 3-5), and Yokosuka plant, Tokyo Electric (Figure 3-6), are listed in Table 3-5. Both use the single-absorber system.

At the Yokosuka plant, Tokyo Electric, limestone is ground in a vertical wet mill (Figure 3-7) to a particle size averaging 25µ. About 90 percent of the limestone charged to the scrubber is reacted with $SO_2$ to recover about 84 percent of the $SO_2$. Sea water is used for gas cooling,

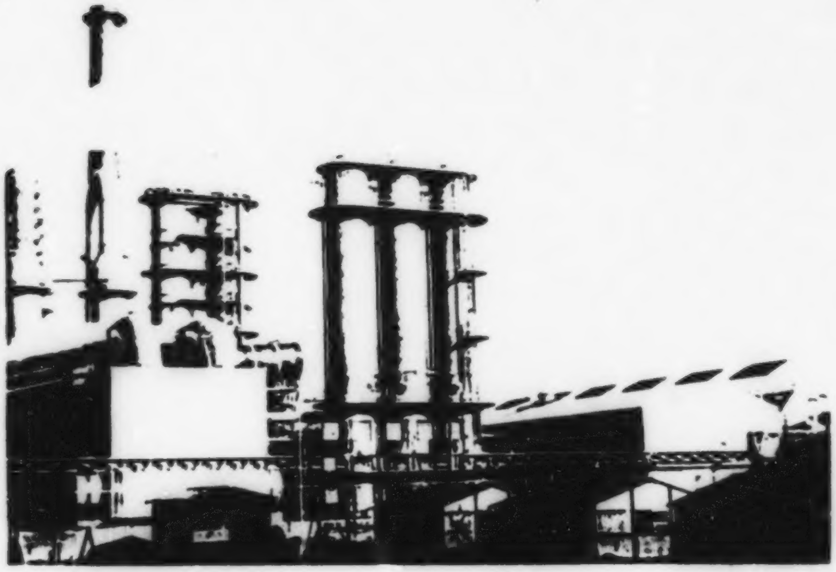


Figure 3-4. Onahama plant, Onahama Smelting.

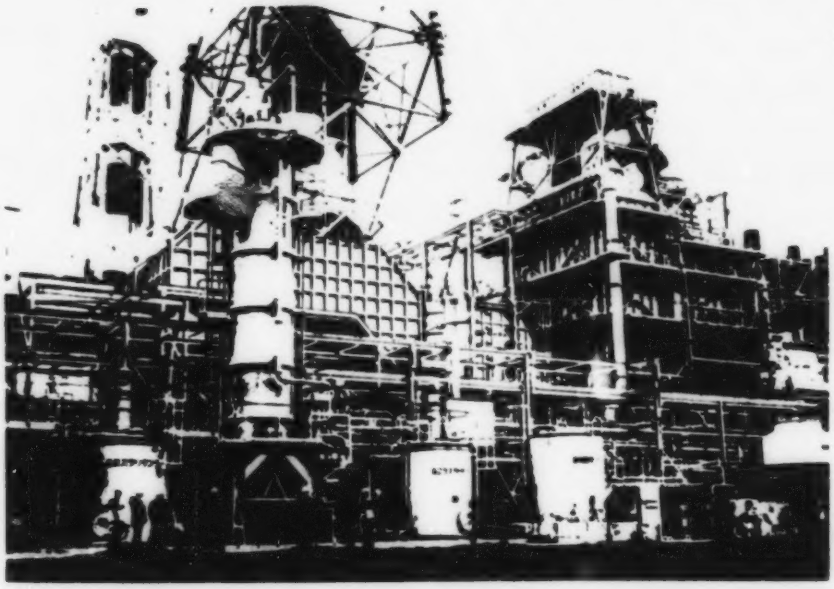


Figure 3-5. Kainan plant, Kansai Electric.

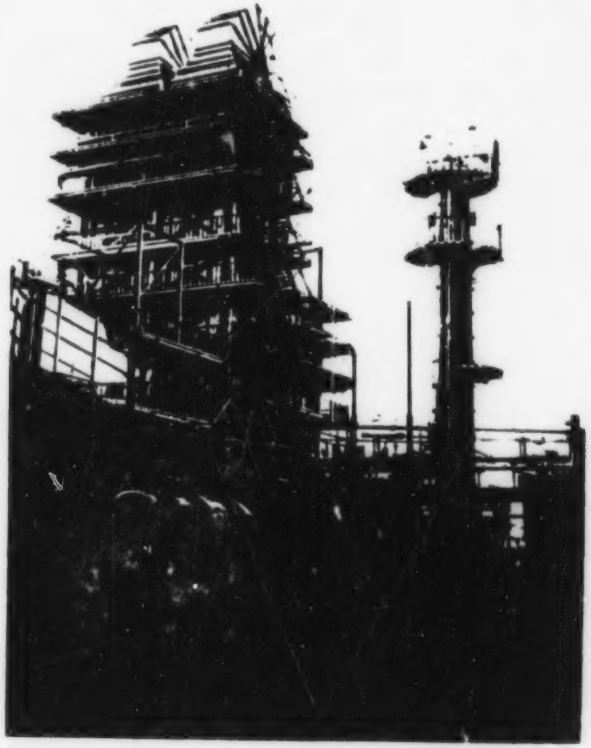


Figure 3-6. Yokosuka plant, Tokyo Electric.

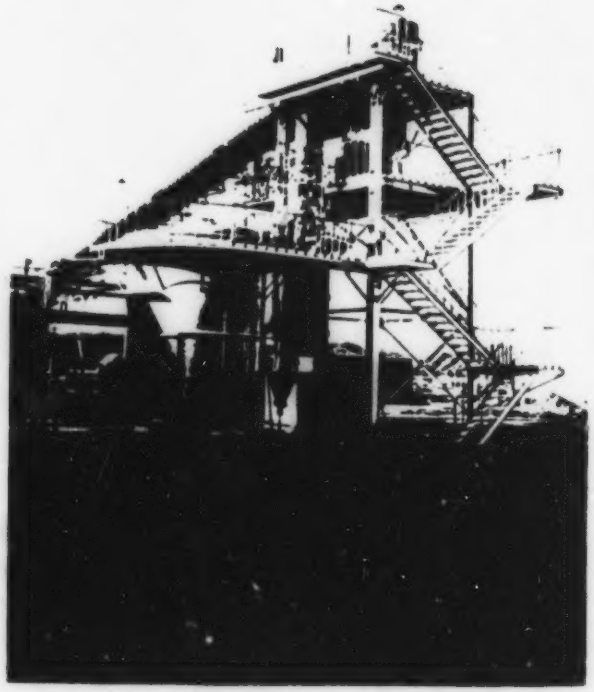


Figure 3-7. Tower mill at Yokosuka plant.

Table 3-5. OPERATION DATA: KANSAI AND TOKYO PLANTS

| | | Kansai Electric, Kainan | Tokyo Electric, Yokosuka |
|---|---|---|---|
| Gas treated, $Nm^3/hr$ | | 400,000 | 400,000 |
| Type of boiler | | Hitachi (600 MW) | CE (265 MW) |
| Load factor, % | | 100 - 80 | 100 - 30 |
| Sulfur in fuel oil, % | | 0.5 - 1 | 0.5 |
| $SO_2$ in flue gas, ppm | | 250 - 550 | 250 |
| $O_2$ in flue gas, % | | 2.4 | 4.7 |
| Absorbent | | $Ca(OH)_2$ | $CaCO_3$ |
| Stoichiometry | | 0.9 - 1 | 0.9 - 1 |
| $SO_2$ recovery, % | | 85 - 95 | 80 - 90 |
| pH of scrubber liquor | | 6 - 7 | 5 - 6 |
| L/G, liters/$Nm^3$ | | 7 | 7 |
| Turndown ratio | | 1/4 | 1/4 |
| Pressure drop, mm $H_2O$ | Cooler | 50 | 50 |
| | Absorber | 30 | 30 |
| | Demister | 20 | 25 |
| Power requirement, kW | | 1,650 | 2,000 |
| Start-up date | | December 1973 | February 1974 |
| Availability since start-up, % | | Over 95 | Over 95 |
| Moisture in gypsum, % | | 8 - 10 | 8 - 10 |
| Use of gypsum | | Cement, board | Board |

and some mist from the cooler goes into the absorber. To prevent the accumulation of chloride, a considerable amount of wastewater is emitted after being treated.

At the Kainan plant, Kansai Electric, industrial water is fed into the cooler. The mist eliminator is washed with a supernatant of the calcium sulfite-gypsum slurry. Technology has been developed for scale-free washing with the saturated solution. Water washing of by-product gypsum (Figure 3-8) is omitted. About 1.5 tons/hr of wastewater are emitted to prevent the accumulation of chloride derived from fuel. The amount of wastewater will be less than that of the by-product gypsum for the new plants that treat flue gas containing more than 1000 ppm $SO_2$. Considerable oxidation of calcium sulfite occurs in the scrubbers of both the Yokosuka and Kainan plants because $O_2/SO_2$ ratios are high. The slurry discharged from the scrubber of the Tokyo plant, Yoshino Gypsum Co., which treats relatively concentrated $SO_2$ (1400 ppm), also contains a considerable amount of gypsum because the gas contains much oxygen. Little oxidation occurs in the absorber of the Onahama plant because of the very high $SO_2$ concentration.

Basic Chemistry and Technology[4]

The reasons for use of a plastic-grid packed tower as the absorber are the large mass transfer coefficient for $SO_2$ absorption, low pressure drop, simple structure, and stability of performance for load variation. MHI has developed formulas for calculation of scrubber size, based on a reaction model in which the dissolution of lime is the rate-determining step:

$$\log \frac{Y_{in}}{Y_{out}} = K\alpha \cdot C_o P_o (1 - \eta) \frac{Z}{G},$$

$$K\alpha = A \cdot C_o^{a} \cdot \left(\frac{L}{G}\right)^{b}$$

where

$Y_{out}$, $Y_{in}$: $SO_2$ concentration at the outlet and inlet, ppm
$P_o$: Gas pressure in scrubber, atm
$C_o$: Effective Ca concentration in slurry, $kg \cdot mole/m^3$
$\eta$: Ca reactivity
Z: Effective height of scrubber, m
G': Superficial gas velocity, $kg \cdot mole/m^2 \cdot h$
L/G: Liquid-gas ratio, liter/$Nm^3$
$K\alpha$: Mass transfer coefficient based on the rate of Ca dissolution, 1/hr atm

In the packed tower, coarse grids are used so as to prevent mesh choking by the slurry. On the basis of the $SO_2$ absorption reaction mechanism mentioned above, grids with large spacing are sufficient from the standpoint of $SO_2$ removal efficiency.

MHI has also studied the oxidation reaction of calcium sulfite. The reaction of equation (1) below is considered to advance through a medium of bisulfite as shown in equations (2) and (3); the reaction mechanism has been proved by correlations among mass transfer coefficient of the oxidizing tower, pH value, and bisulfite ion concentration, as shown in Figure 3-9.

$$CaSO_3 \cdot 1/2\ H_2O + 1/2\ O_2 + Aq = CaSO_4 \cdot 2H_2O + Aq \qquad (1)$$

$$HSO_3^- + 1/2\ O_2\ \text{(in solution)} = SO_4^{2-} + H^+ \qquad (2)$$

$$CaSO_3 \cdot 1/2\ H_2O + H^+ = Ca^{2+} + HSO_3^- + 1/2\ H_2O \qquad (3)$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O \qquad (4)$$

Figure 3-8. By-product gypsum at Kainan plant, Kansai Electric.

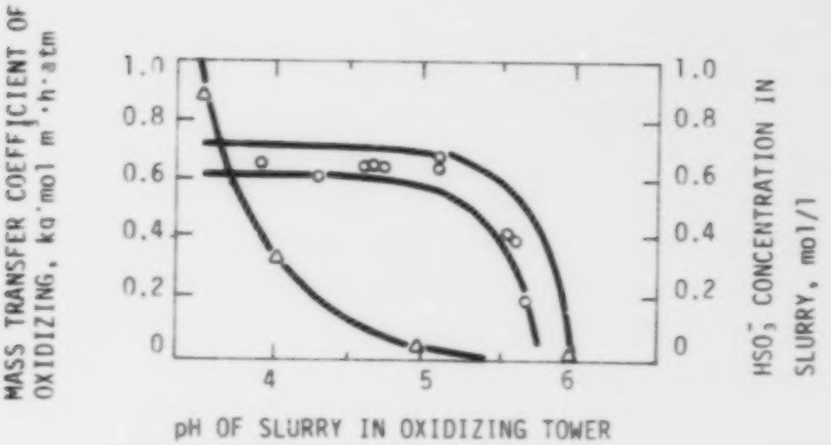


Figure 3-9. Influence of slurry pH on oxidation rate and HSO$_3^-$ concentration.

## Evaluation

Stable operation of the Mitsubishi-JECCO process has been well demonstrated. High $SO_2$ recovery and good quality of salable gypsum are other advantages. The capital and operating costs are estimated to be lower than those of the double-alkali and Wellman-Lord processes. Because of these features, MHI is the leading constructor of desulfurization plants in Japan. The plant cost, however, has now reached $60/kW. Further simplifications, such as reduction of the size of the cooler, may be desirable.

MHI has recently started tests with flue gas from a coal-fired boiler. The results should indicate the applicability of the process in the U.S.

Although the total amount of water leaving the system as moisture in gypsum and wastewater is about equal to that being discarded in the U.S in sludge that contains about 50 percent water, the volume of wastewater should be further reduced or eliminated for application in the U.S. Use of sulfuric acid should be also eliminated; this may be achieved by use of the two-tower system.

## CHEMICO-MITSUI AND MITSUI MIIKE LIME-LIMESTONE PROCESSES

### State of Development

Mitsui Miike Machinery Co. has constructed a desulfurization unit using Chemico scrubbers at the Omuta plant, Mitsui Aluminum Co. (Figure 3-10). This plant has operated smoothly since its start-up in April 1972 treating a flue gas from a 156-MW coal-fired boiler to by-produce a calcium sulfite sludge (Figure 3-11). Because of the limited landspace available for discarding the sludge, Mitsui Miike has recently developed a process to produce gypsum by using limestone as the absorbent along with a catalyst to promote the reaction. The reason for the use of limestone is the low cost and the shortage of carbide sludge at the Omuta plant. A prototype plant (25 MW equivalent) started operation in

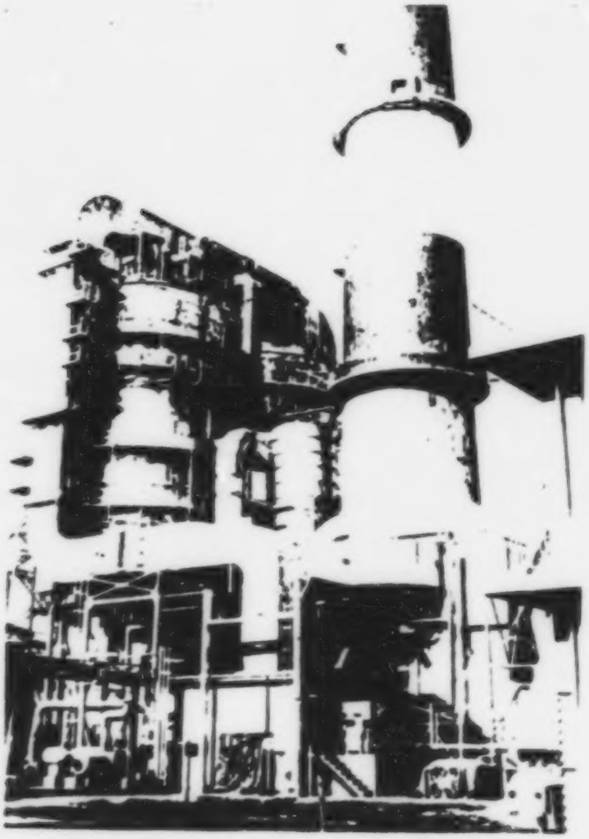


Figure 3-10. Omuta plant, Mitsui Aluminum.

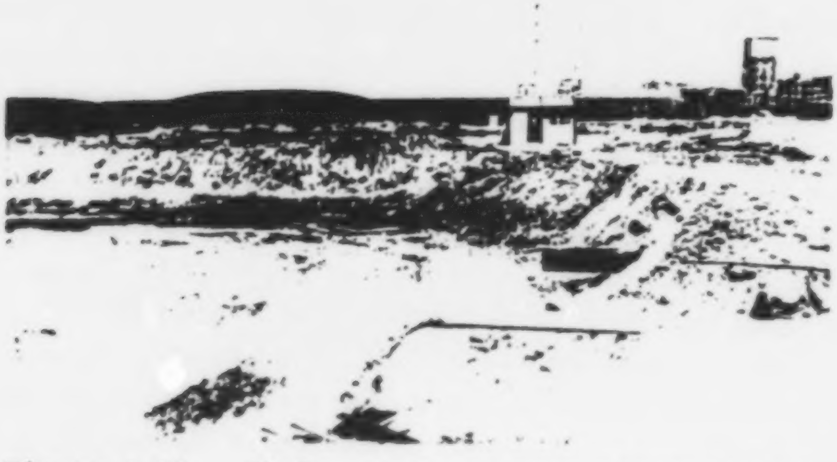


Figure 3-11. Sludge pond at Omuta plant, Mitsui.

October 1974 at the Omuta facility. Four commercial plants are under construction (Table 3-6). All use Chemico scrubbers to treat flue gas from coal-fired boilers.

### Description

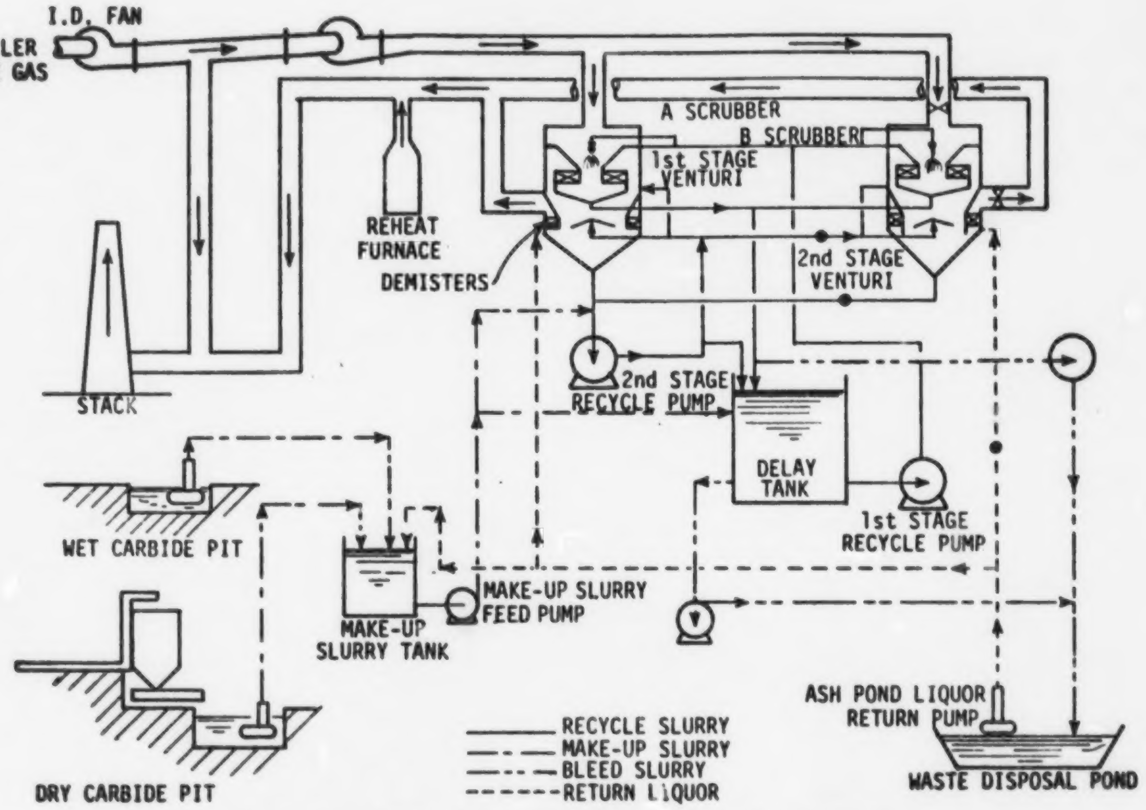
A flowsheet of the first operation of the Chemico-Mitsui process generating calcium sulfite sludge is shown in Figure 3-12. Some of the operation parameters are shown in Table 3-2. Because this plant is familiar in the United States, having been described by many people,[5,3] further description is not needed here except for noting of a recent finding by the author. X-Ray and microscopic tests of the calcium sulfite sludge discharged from the scrubber indicated the absence of gypsum, although chemical analysis of the solids shows that 5 to 10 percent oxidation occurred. This finding indicates the possibility that some of the $SO_3^=$ ions in calcium sulfite are replaced by $SO_4^=$ ions and supports the theory of "unsaturated mode operation" proposed by Borgwardt.[2] Although the solution may be saturated with the solids formed by the replacement, it is not saturated with gypsum and thus the possibility of scaling is minimized. The X-ray diffraction pattern is shown in Figure 3-13 in comparison with that of a solid containing some gypsum.

A flowsheet of the Mitsui Miike limestone-gypsum process is shown in Figure 3-14. Flue gas is treated in two venturi scrubbers in series with a countercurrent flow of limestone slurry containing a metallic catalyst. The resulting calcium sulfite slurry is then fed into a pH controller, where the slurry contacts a portion of flue gas (5 to 10 percent of the total) to lower the pH and to complete the reaction of limestone with $SO_2$. The slurry is then pumped into an oxidizing tower, into which air is blown from the bottom to convert the sulfite into gypsum. The gypsum slurry is centrifuged. Most of the liquor from the centrifuge is used to prepare a limestone slurry. A small portion of the liquor is sent to a wastewater treatment system to prevent the accumulation of impurities.

Table 3-6. PLANTS USING THE MITSUI MIIKE LIMESTONE PROCESS

| User | Plant site | Capacity, MW | $SO_2$, ppm | | Dust, $g/Nm^3$ | | Year of completion |
|---|---|---|---|---|---|---|---|
| | | | In | Out | In | Out | |
| Mitsui Aluminum | Omuta | 25 | 2,350 | 200 | 0.6 | 0.06 | Nov. 1974 |
| EPDC[a] | Takasago | 250 | 1,500 | 100 | 0.1 | 0.05 | Jan. 1975 |
| EPDC | Takasago | 250 | 1,500 | 100 | 0.1 | 0.05 | Oct. 1975 |
| Mitsui Aluminum | Omuta | 175 | 1,930 | 190 | 0.6 | 0.06 | April 1975 |
| Mitsui Aluminum | Omuta | 156 | 2,000 | 200 | 0.6 | 0.06 | Sept. 1975 |

[a] Electric Power Development Co.


I.D. FAN
BOILER FLUE GAS
STACK
REHEAT FURNACE
DEMISTERS
A SCRUBBER
B SCRUBBER
1st STAGE VENTURI
2nd STAGE VENTURI
2nd STAGE RECYCLE PUMP
DELAY TANK
1st STAGE RECYCLE PUMP
WET CARBIDE PIT
DRY CARBIDE PIT
MAKE-UP SLURRY TANK
MAKE-UP SLURRY FEED PUMP
ASH POND LIQUOR RETURN PUMP
WASTE DISPOSAL POND
RECYCLE SLURRY
MAKE-UP SLURRY
BLEED SLURRY
RETURN LIQUOR

NOTE: ONLY ONE SCRUBBER SYSTEM PRESENTLY IN OPERATION.

● INDICATES A CLOSED VALVE

⋈ INDICATES A CLOSED DAMPER

Figure 3-12. Flowsheet of Chemico-Mitsui lime process (Omuta).

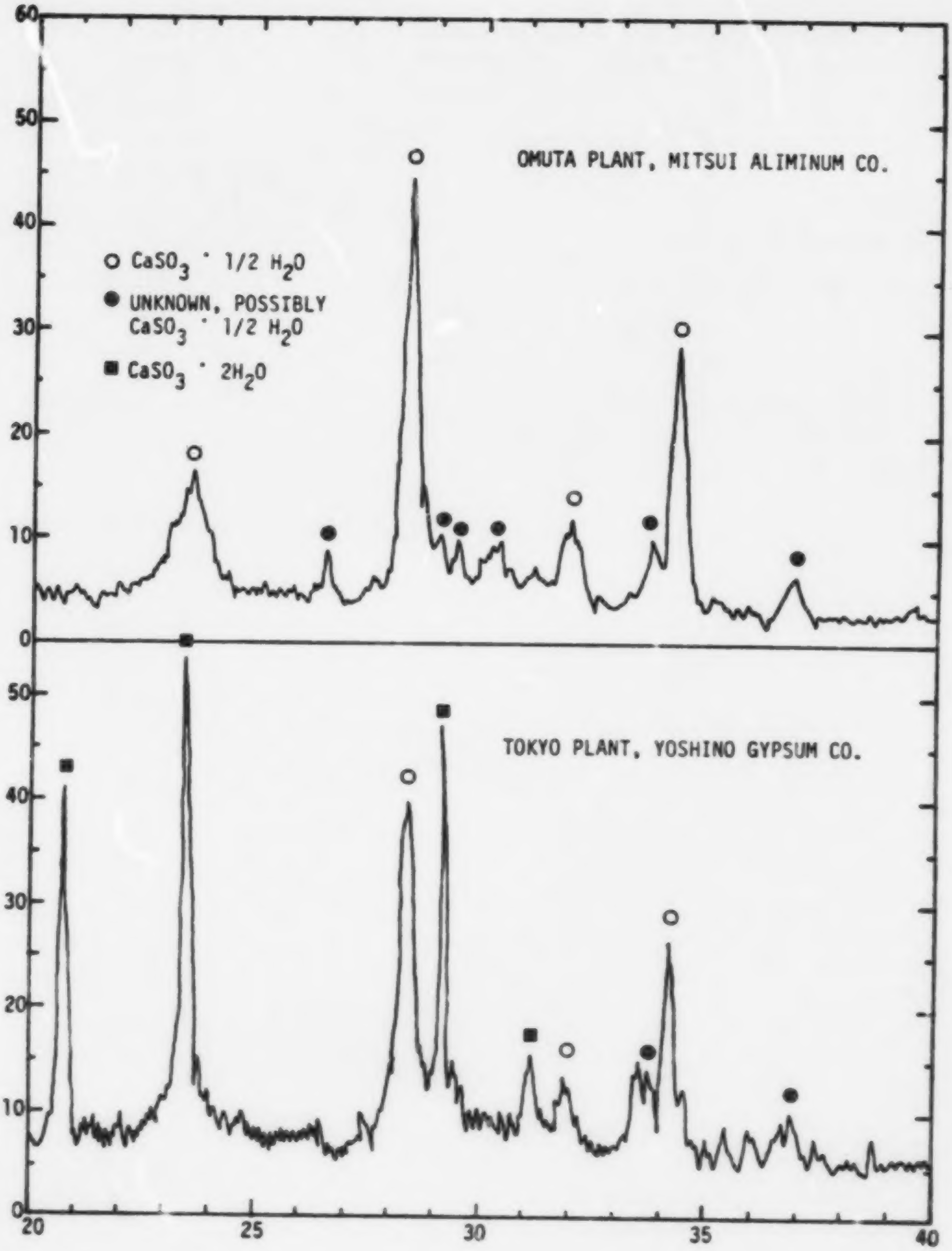


Figure 3-13. X-Ray diffraction pattern of sludge from scrubber.

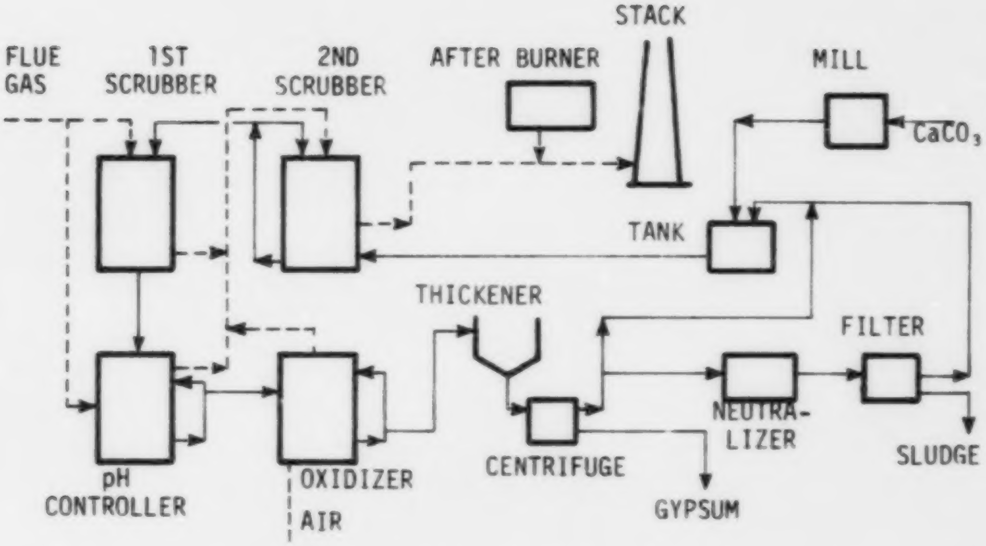

STACK
FLUE GAS
1ST SCRUBBER
2ND SCRUBBER
AFTER BURNER
MILL
$CaCO_3$
TANK
THICKENER
FILTER
NEUTRALIZER
SLUDGE
CENTRIFUGE
pH CONTROLLER
OXIDIZER
AIR
GYPSUM

Figure 3-14. Flowsheet of Mitsui Miike limestone-gypsum process.

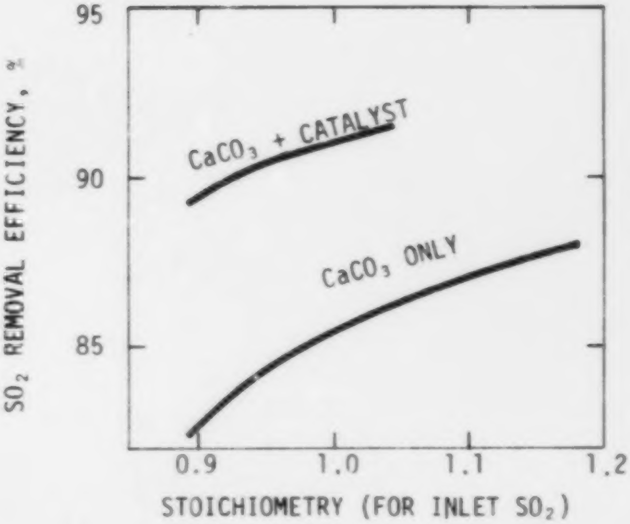


Figure 3-15. Effect of catalyst on $SO_2$ removal efficiency.

The catalyst prevents the formation of a calcium sulfate coating on calcium sulfite and carbonate and thus promotes both the reaction of the carbonate with $SO_2$ and the oxidation of the sulfite into sulfate, as shown in Figure 3-15 and Table 3-7, which are based on pilot tests. There is virtually no loss of catalyst into gypsum because gypsum can be washed well. In the wastewater treatment, the catalyst can be precipitated in the form of hydroxide by raising the pH. The catalyst thus can be returned to the absorbing system.

Table 3-7. EXAMPLE OF THE COMPOSITION OF BY-PRODUCT (stoichiometry 0.95; values in percent)

| Absorbent | $CaSO_4 \cdot 2H_2O$ | $CaSO_3$ | $CaCO_3$ |
|---|---|---|---|
| $CaCO_3$ + Catalyst | 98.2 | 0.7 | trace |
| $CaCO_3$ only | 71.0 | 15.3 | 12.3 |

Since its start-up, the prototype plant at Omuta has been operated smoothly. Tests of the by-product gypsum for wallboard production have shown that although the gypsum is pure enough and useful, further improvement of the crystal shape is desirable for higher strength. The by-product from the Takasago plant, Electric Power Development Company (EPDC) will be used for cement.

## Evaluation of the Process

The Chemico-Mitsui lime-calcium sulfite process at the Omuta plant has proved to be highly reliable because of the unsaturated-mode operation. Sludge disposal, however, is a big problem in Japan. The Mitsui Miike process has an advantage of producing usable gypsum requiring no sulfuric acid and might suit U.S. application. But the capital required is about 50 percent higher for the lime-calcium sulfite process. Where cheap sulfuric acid is available, a simpler oxidizing system using a small amount of sulfuric acid could be more economical. If about 80 percent oxidation is sufficient to improve the properties of the sludge, the oxidizing system may be much simplified. The sludge pond should be sealed to prevent leakage of water containing the catalyst.

## BABCOCK-HITACHI PROCESS

### State of Development

Hitachi Ltd. has constructed a desulfurization unit at Mizushima Station, Chugoku Electric, using the Babcock and Wilcox process. The unit has a capacity of treating 320,000 $Nm^3$/hr of flue gas from an oil-fired boiler. The process by-produces salable gypsum. The unit was put in operation in November 1973. Hitachi is now constructing four plants, as shown in Table 3-8. A scrubber unit is used for each plant except the Tamashima plant, Chugoku Electric, which will install four units, three for normal use and one for backup.

### Process Description

The scrubber is of the standard B and W type, a venturi followed by a perforated plate absorber (Figure 3-16). The venturi serves as a cooler and humidifier rather than a dust removal unit. A limestone slurry, 105 to 110 percent of stoichiometric amount, is used. The pH of the circulating slurry in the absorber is 6.2, the L/G ratio 7 liters/$Nm^3$ (50 gal./1000 scf), the gas velocity 2 m/sec, and the solids concentration 7 to 8 percent. The treated gas is passed through a mist eliminator (one-pass, four-section chevron with a trap-out tray below it). Total pressure drop is 750 mm $H_2O$. The wash liquor from the eliminator is circulated from the tray to the thickener and back to the mist eliminator again. A portion of the calcium sulfite slurry from the circulation tank is sent continuously to a reactor to convert the remaining calcium carbonate into gypsum by

Table 3-8. PLANTS USING THE BABCOCK-HITACHI PROCESS

| User | Plant site | Capacity,[a] | | $SO_2$, ppm | | Year of completion |
|---|---|---|---|---|---|---|
| | | MW | 1000 $Nm^3$/hr | Inlet | Outlet | |
| Chugoku Electric | Mizushima | 105 | 320 | 400 | 40 | Nov. 1973 |
| Asahi Chemical | Mizushima | 150 | 481 | 1480 | 50 | Mar. 1975 |
| Kansai Electric | Osaka | 160 | 500 | 550 | 50 | Apr. 1975 |
| Chugoku Electric | Tamashima | 500 | 1480[b] | 1500 | 50 | June 1975 |
| Kansai Electric | Osaka | 160 | 500 | 550 | 50 | Jan. 1976 |

[a] All from oil-fired boilers.

[b] Four scrubbers.

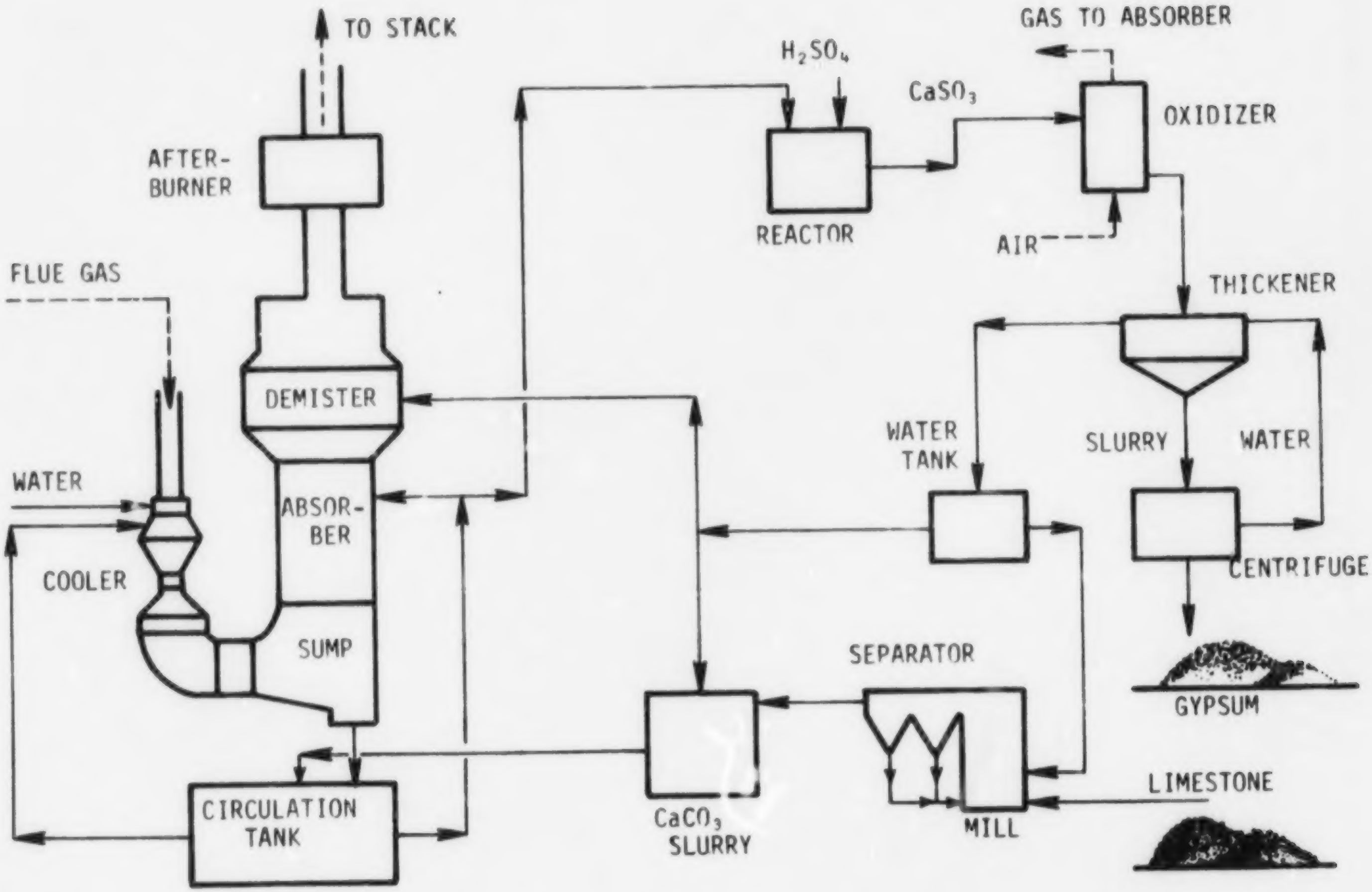

TO STACK
AFTER-
BURNER
FLUE GAS
WATER
COOLER
DEMISTER
ABSOR-
BER
SUMP
CIRCULATION
TANK
$H_2SO_4$
$CaSO_3$
REACTOR
GAS TO ABSORBER
OXIDIZER
AIR
THICKENER
WATER
TANK
SLURRY
WATER
CENTRIFUGE
GYPSUM
SEPARATOR
MILL
LIMESTONE
$CaCO_3$
SLURRY

Figure 3-16. Flowsheet of Babcock-Hitachi limestone-gypsum process.

adding sulfuric acid and then is fed into an oxidizer, which uses a JECCO rotary atomizer. The gypsum is centrifuged, and the product gypsum, containing 7 to 8 percent moisture, is sold.

### Performance

The Mizushima plant (Figure 3-17) underwent test operation for 5 months following its start-up in November 1973. There was some trouble with solids deposition in the sump below the venturi and the absorber. This problem has been eliminated by modifying the structure. In addition, a deposit of fine-grained scale (0.2 mm) formed on the ID fan and caused a vibration. The fan is now being washed. For the new plants to be built, a booster fan will be used in place of the ID fan.

Commercial operation started in April 1973, and plant availability since that time has reached 96 percent. Inlet $SO_2$ concentrations range from 300 to 500 ppm and outlet concentrations from 20 to 50 ppm. Oxidation of sulfite in the scrubber reaches 90 percent because of the low $SO_2$ concentration and high $O_2$ concentration (5%). Energy consumption is about 2.3 percent for the scrubber system and 2.5 percent for reheat. The make-up water (19 t/hr) is added to the clarifier overflow tank. Of the 19 tons, 4 tons is bled from the system to prevent accumulation of impurities such as chloride and magnesium.

### Evaluation

Operation of the Mizushima plant, Chugoku Electric, seems to be fairly good, but the $SO_2$ concentration is low and the amount of wastewater is relatively large. Opportunities for further evaluation will be afforded by operation of the plants of Asahi Chemical (Mizushima plant) and Chugoku Electric (Tamashima plant), which will start during 1975 to treat flue gas containing about 1500 ppm $SO_2$.

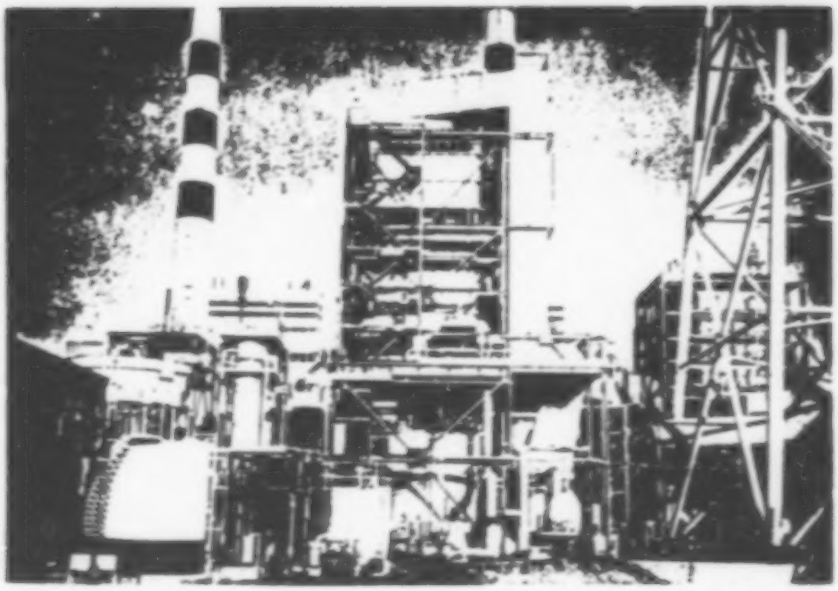


Figure 3-17. Mizushima plant, Chugoku Electric.

## CHUBU-MKK PROCESS (CM PROCESS)

### State of Development

Mitsubishi Chemical Machinery (MKK) jointly with Chubu Electric Power, has developed a wet-lime/limestone process using a screen type scrubber. The first commercial plant using a limestone slurry was built at Yokkaichi plant, Ishihara Industries, and went into operation in March 1974. The unit has a capacity of treating 250,000 $Nm^3$/hr of flue gas from oil-fired boilers. The second plant using a lime slurry is near completion at the Yokkaichi plant, Mitsubishi Gas, with a capacity of treating 70,000 $Nm^3$/hr of flue gas from an oil-fired boiler.

### Process Description

A flowsheet of the unit for Ishihara Industries is shown in Figure 3-18. Flue gas is first cooled with a water spray and then introduced into an absorber, which has a spray in the lower part and several screens set at an angle in the upper part. A limestone slurry (3 to 10 percent solids) flows on the screens forming liquid films, which absorb $SO_2$. Gas velocity in the scrubber (4 by 4.8 by 16.8 m, stainless steel) is about 4 m/sec and the pressure drop is 200 mm $H_2O$. The pH of the slurry into the absorber is 6.2 to 6.3 and that of the effluent nearly 6. A stoichiometric amount of limestone (minus 325 mesh) is used to remove about 90 percent of the $SO_2$ (1300 ppm). The L/G ratio in the scrubber is about 10 liters/$Nm^3$. As the flue gas contains about 5 percent oxygen, about 40 percent of the calcium sulfite is oxidized in the absorber into gypsum. A portion of the slurry from the absorber is sent to an oxidizer after pH adjustment with sulfuric acid and oxidized into gypsum with air by use of a JECCO rotary atomizer.

The gas leaving the absorber is passed through a mist eliminator and heated by an afterburner to 120°C. The oil consumption is about 5 percent of the oil for boilers. The mist eliminator (chevron type) is washed with fresh water.

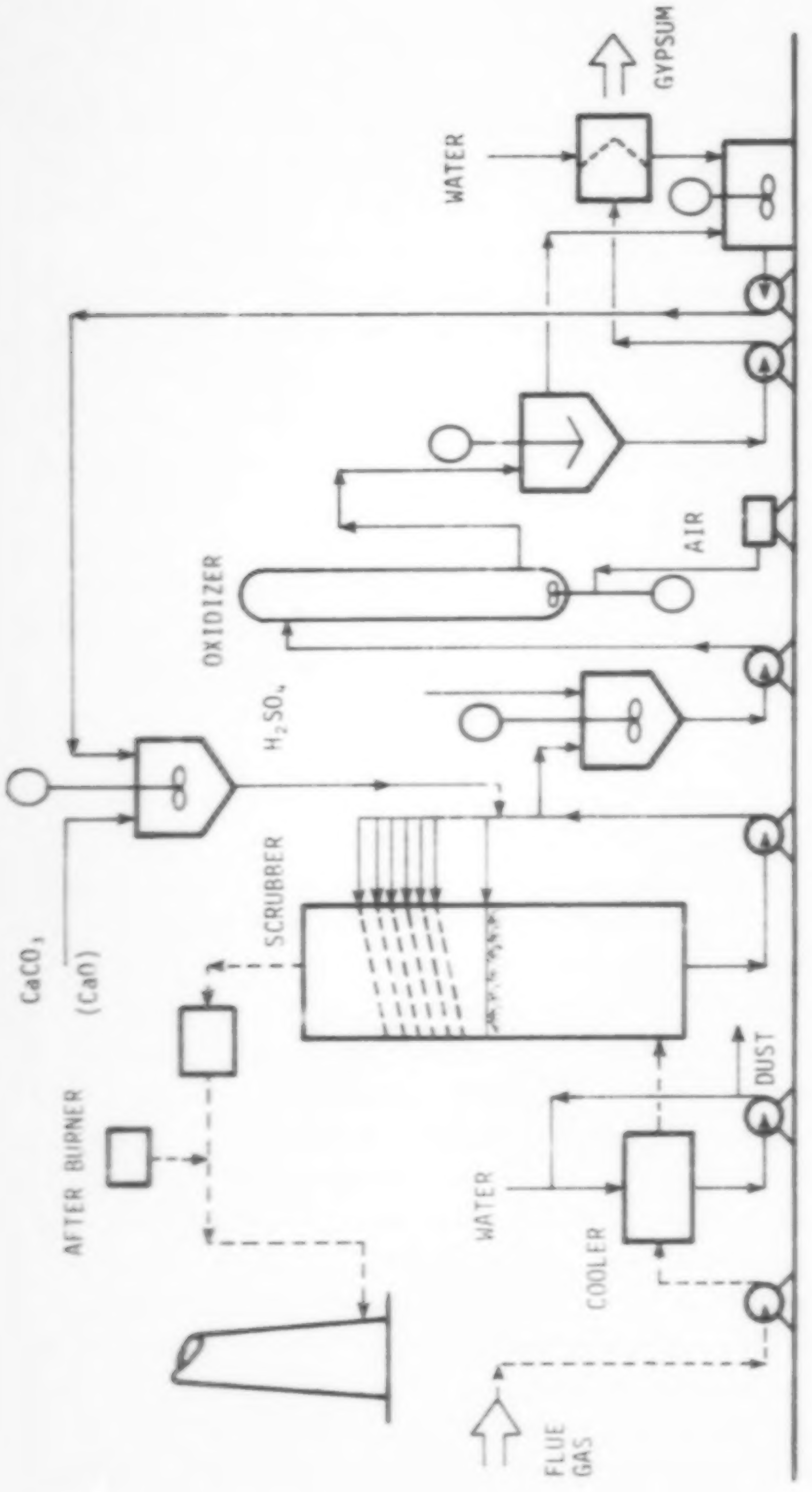

FLUE GAS
COOLER
WATER
DUST
AFTER BURNER
$CaCO_3$
($CaO$)
SCRUBBER
$H_2SO_4$
OXIDIZER
AIR
WATER
GYPSUM

Figure 3-18. Flowsheet of CM process (Ishihara Chemical).

About 20 t/hr water is fed into the cooler, in which 16 t/hr is volatilized. The difference, about 4 t/hr, is discharged from the system after being treated. The mist eliminator is washed intermittently with fresh water. Considerable portions of the mother liquor of gypsum slurry and wash water of gypsum are also discarded. The by-product gypsum, about 50 t/day, is sold for wallboard production.

### Evaluation

The process is simple and can attain 90 percent removal of $SO_2$ using limestone. Some scaling problems occurred, mainly on the wall of the scrubber, in the early operation period. To prevent the scaling Ishihara seems to use much fresh water, which results in the emission of much wastewater. Further improvement would be required to reduce the amount of wastewater.

The plant cost 810 million yen ($2.7 million, as of 1973). The Wellman-MKK process plant at Chubu Electric Power (620,000 $Nm^3$/hr) cost 2000 million yen at an even earlier period. MKK estimates that the Wellman-MKK process would cost about one-third more than the limestone scrubbing process.

## KOBE STEEL CALCIUM CHLORIDE PROCESS (CAL PROCESS)

### State of Development

Kobe Steel Ltd. has developed a process which uses a 30 percent calcium chloride solution dissolving lime as an absorbing liquor. A pilot plant with a capacity of treating 50,000 $Nm^3$/hr of waste gas from an iron ore sintering plant was operated from June to December 1974. Two commercial plants, each with a capacity of treating 375,000 $Nm^3$/hr of waste gas from iron ore sintering, are to be completed soon--one at Amagasaki Works, Kobe Steel, in November 1975, and the other at Nadahama Works, Kobe Steel, in January 1976.

## Process Description

A flowsheet of the process is shown in Figure 3-19. Waste gas is first cooled in a cooler to which calcium chloride solution (about 5 percent, from a gypsum centrifuge) is fed to cool the gas to about 70°C and to remove most of the dust. The solution is concentrated to about 30 percent and is sent to a scrubber system after dust removal by filtration. The gas is then led into an absorber in which a calcium chloride solution (about 30 percent, at pH 7 dissolving lime) is sprayed to remove more than 90 percent of the $SO_2$. The gas is then passed through a mist eliminator and sent to a stack. The liquor discharged from the absorber at pH 5.5, containing calcium sulfite, is sent to a centrifuge to separate most of the solution, which is sent to a tank where calcium hydroxide is dissolved to raise the pH to 7. The calcium sulfite sludge from the centrifuge is repulped with water and some sulfuric acid to produce a slurry at pH 4. The slurry is oxidized by air bubbles into gypsum, which is then centrifuged. The liquor from the centrifuge, containing about 5 percent calcium chloride, is returned to the cooler.

## Theory

Calcium chloride solution can dissolve 6 to 7 times as much lime as does water (Figure 3-20). The solution containing lime absorbs $SO_2$ more rapidly but $CO_2$ and $O_2$ more slowly than does milk of lime. High $SO_2$ removal can be attained using a relatively low L/G ratio (Figures 3-21 and 3-22). The vapor pressure of the solution is low (Figure 3-23); less water is evaporated in the cooler and absorber and thus the temperature of the liquor in the absorber reaches 70°C, as compared with 55 to 60°C in usual wet processes. The temperature of the treated gas is higher, resulting in a smaller energy requirement for reheating. Calcium chloride reduces the oxidation of calcium sulfite.

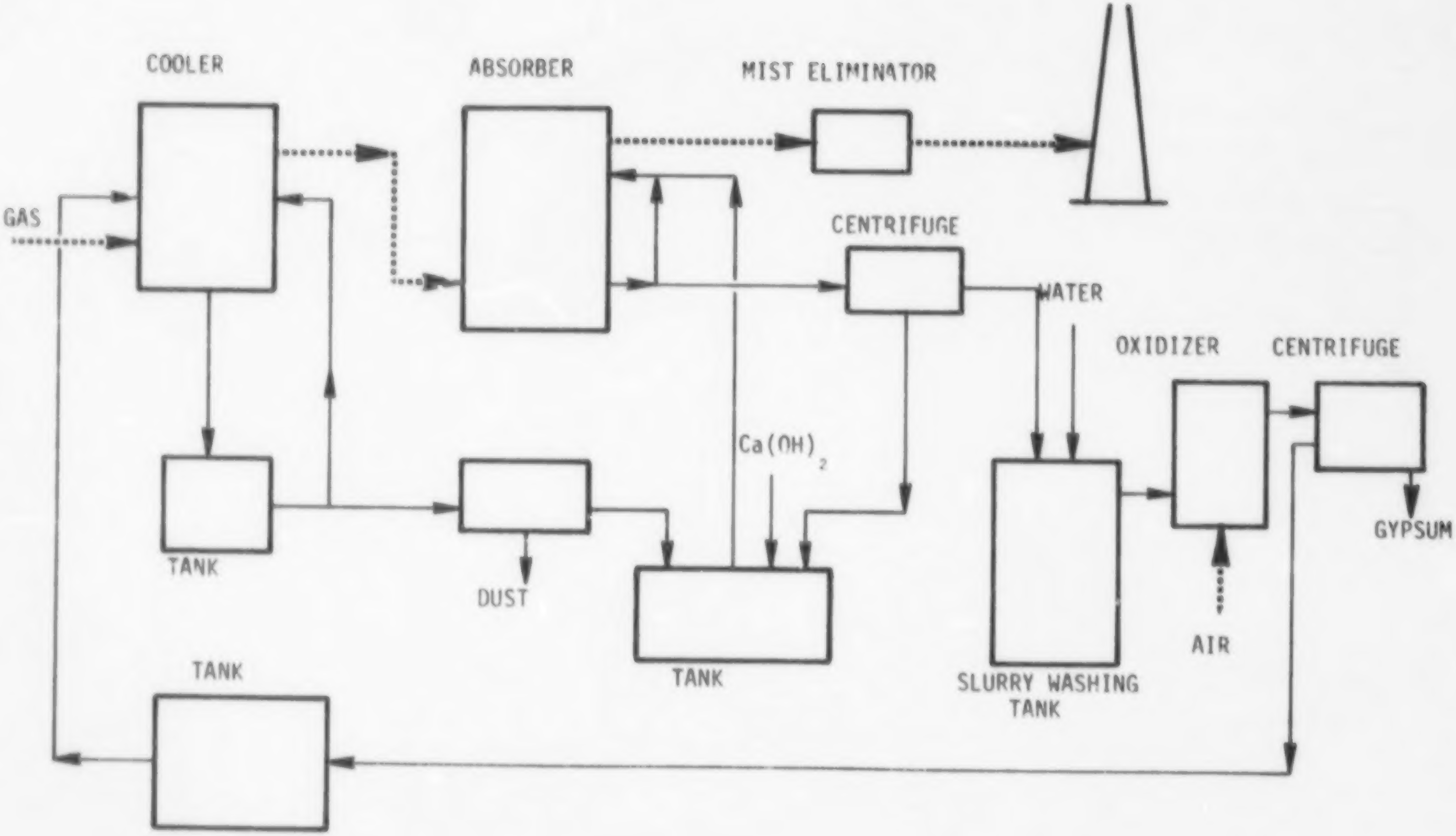

COOLER
ABSORBER
MIST ELIMINATOR
GAS
CENTRIFUGE
WATER
OXIDIZER
CENTRIFUGE
Ca(OH)$_2$
TANK
DUST
TANK
SLURRY WASHING TANK
AIR
GYPSUM
TANK

Figure 3-19. Flowsheet of Kobe Steel process (Cal process).

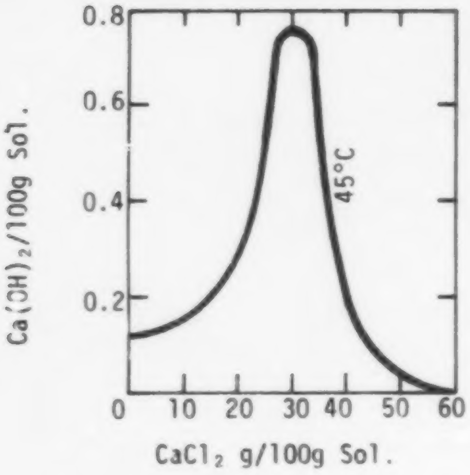


Figure 3-20. Solubility of lime in calcium chloride solution.

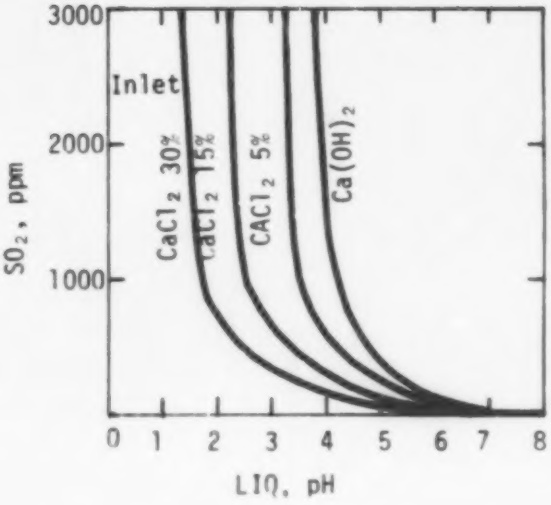


Figure 3-21. Vapor pressure of $SO_2$.

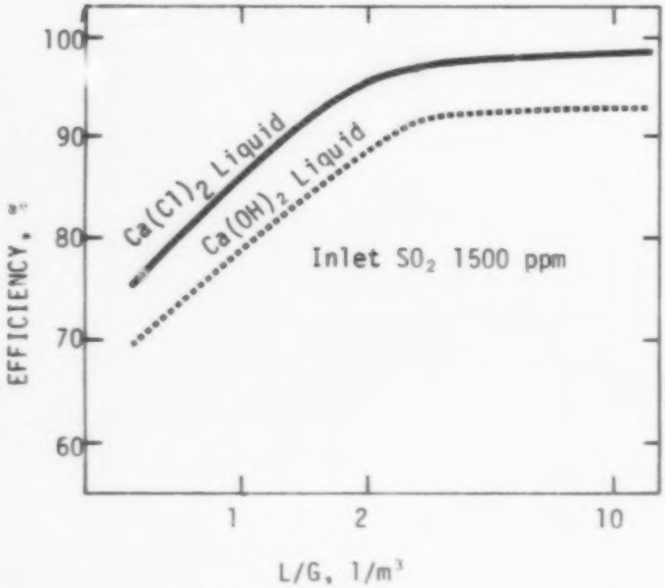


Figure 3-22. L/G and $SO_2$ removal efficiency.

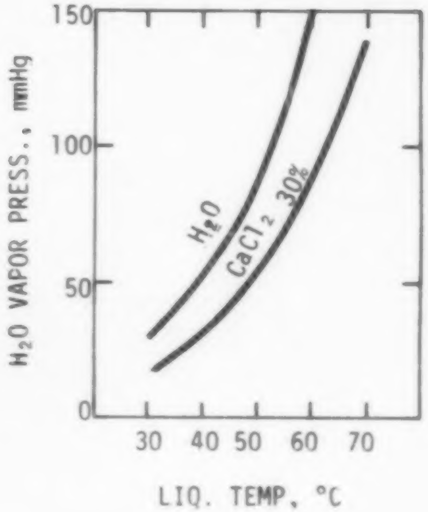


Figure 3-23. Vapor pressure of $H_2O$.

## Operation

The pilot plant was operated nearly continuously from June 1974 to the end of the year, treating mainly waste gas from an iron ore sintering plant containing 200 to 400 ppm $SO_2$ and 15 to 16 percent $O_2$. About 90 percent of the $SO_2$ is removed at an L/G ratio of 2. At a ratio of 1, scaling occurred on the wall of the absorber, but operation at L/G 2 or higher could prevent it. Oxidation of calcium sulfite in the absorber is rather low (about 30 percent) for the high oxygen and low $SO_2$ concentrations because of the effect of the chloride. The reason for use of the calcium sulfite centrifuge is to reduce the calcium chloride concentration in the oxidizer; the oxidation occurs fairly rapidly at the 5 percent concentration. The centrifuged gypsum is not washed with water and contains about 10 percent liquor (about 0.5 percent calcium chloride) but is useful as retarder of cement setting.

Corrosion has been the main problem. Stainless steel, plastic, and rubber linings are used for the material. Because the lower part of the cooler where the hot gas is introduced was corroded severely, the part was replaced by titanium, which is durable.

The mist eliminator is washed intermittently with the calcium chloride solution. Because calcium chloride is hygroscopic, the eliminator always keeps wet; although some solid matter is deposited on the eliminator, it does not form hard scale and can be washed away. No wastewater was purged during the 6 months' operation, although some liquor was lost when the rubber lining of pumps was repaired. Concentrations of magnesium and other impurities increased in the liquor but caused no problem.

## Evaluation

The process has the following advantages and disadvantages as compared with other wet-lime processes. Advantages: (1) high $SO_2$ removal efficiency, (2) relatively high outlet gas temperature, (3) no need for sulfuric acid addition for pH control prior to the oxidation, and (4) use of low L/G ratio and less water. Disadvantages: (1) need of a thickener and two centrifuges, and (2) greater corrosion problem.

Although the pilot plant was operated without scaling and wastewater problems, further evaluation must await operation of a larger plant with a higher concentration of $SO_2$ over a longer period.

## SUMITOMO-FUJI KASUI PROCESS (MORETANA PROCESS)

### State of Development

Sumitomo Metal Industries Ltd. has developed a lime/-limestone process jointly with Fuji Kasui Kogyo K. K. using the Moretana scrubber, which is a sort of perforated plate scrubber. A test plant with a capacity of treating 62,000 $Nm^3/hr$ of flue gas from an oil-fired boiler has been operated at the Amagasaki plant, Sumitomo Metal, since May 1973. Several commercial plants have recently been completed or are now under construction, as shown in Table 3-9.

Table 3-9. PLANTS USING THE MORETANA PROCESS

| User | Plant site | Gas treated, $Nm^3/hr$ | Source of gas | Completion |
|---|---|---|---|---|
| Sumitomo Metal | Amagasaki | 62,000 | Boiler | May 1973 |
| Sumitomo Metal | Wakayama | 25,000 | S.P.[a] | June 1974 |
| Ide Paper | Fuji | 60,000 | Boiler | Dec. 1974 |
| Yokohama Rubber | Onomichi | 29,000 | Boiler | Dec. 1974 |
| Sumitomo Metal | Wakayama | 370,000 | S.P.[a] | Jan. 1975 |
| Sumitomo Metal | Kokura | 92,000 | H.F.[b] | Apr. 1975 |
| Sanyo Kokusaku Pulp | Kozu | 140,000 | Boiler | Apr. 1975 |
| Meiji Seika | Ashigara | 30,000 | Boiler | Apr. 1975 |

[a] Iron ore sintering plant.

[b] Heating furnace.

## Process Description

A flowsheet of the process is shown in Figure 3-24. Flue gas passing through an electrostatic precipitator is cooled in a prequench scrubber and then introduced into a main scrubber (Moretana scrubber). The treated gas is passed through a mist eliminator and an oil-fired reheater. Lime or limestone slurry is fed to the main scrubber. The bleed stream of the reacted slurry is treated with sulfuric acid to reduce pH and sent to an oxidizer designed by Fuji Kasui. Calcium sulfite is oxidized by air or oxygen into gypsum, which is centrifuged.

## Status of Technology

The Moretana scrubber is fitted with four perforated plates made of stainless steel. The holes range from 6 to 12 mm in diameter and the plates are 6 to 20 mm thick. Both dimensions are varied depending on the specific scrubbing situation. The free space in the cross section ranges from 25 to 50 percent. The bottom tray serves mainly as a gas distributor and the upper three serve as absorbers. The gas and liquid flows are so adjusted as to maintain a liquor head of 10 to 15 mm on each plate. The gas velocity is higher than in usual scrubbers. The design gives extreme turbulence, producing a foam layer 400 to 500 mm thick. The mist eliminator is a set of vertical chevron sections mounted in a horizontal duct after the scrubber. Design data for the Amagasaki plant, Sumitomo Metal, are as follows:

| | |
|---|---|
| L/G ratio | 5.4 liters/$Nm^3$<br>(about 40 gal./1000 scf) |
| Gas velocity in scrubber | 4 to 5 m/sec |
| Solids content of slurry | 3 to 8 percent |
| pH | inlet: 8.5 - 8.8<br>outlet: 6.5 - 6.7 |
| Stoichiometry | 1.05 - 1.2 |
| Fresh water make-up | 15 t/hr |

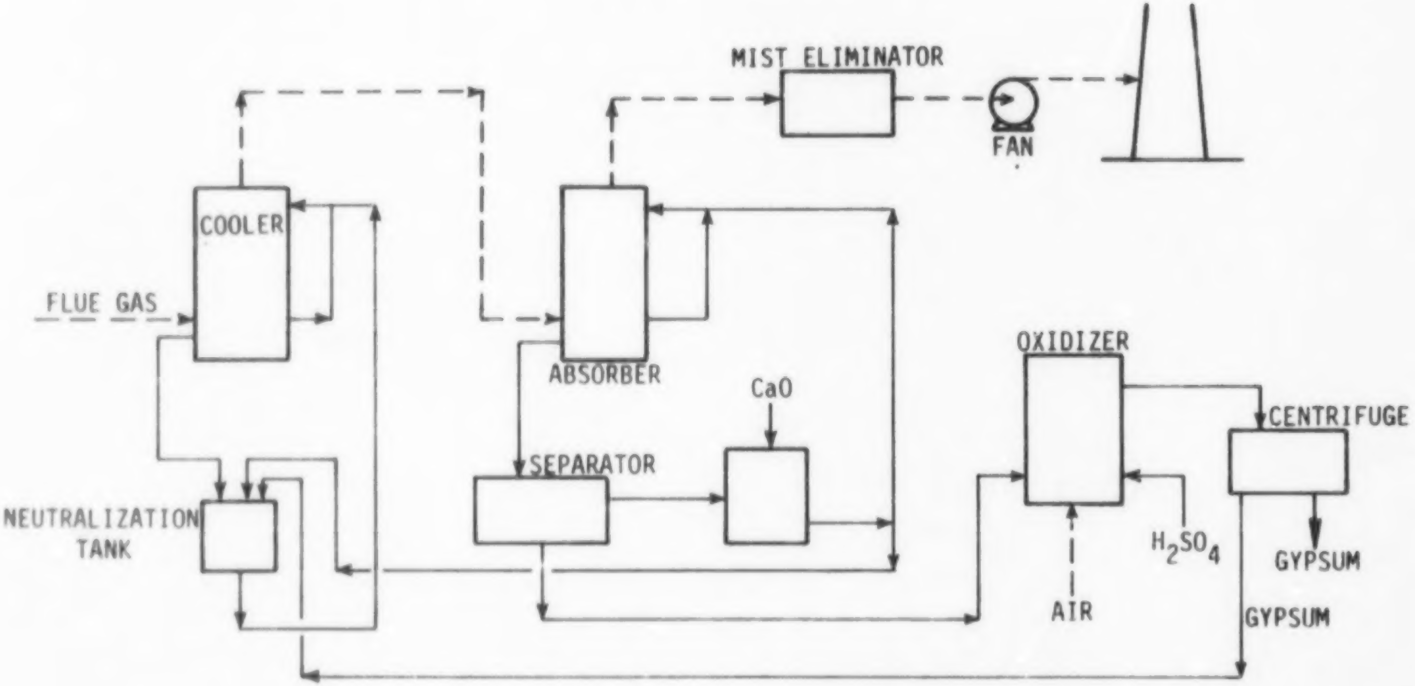

MIST ELIMINATOR
FAN
COOLER
FLUE GAS
ABSORBER
CaO
OXIDIZER
CENTRIFUGE
SEPARATOR
NEUTRALIZATION TANK
$H_2SO_4$
GYPSUM
AIR
GYPSUM

Figure 3-24. Simplified flowsheet of Moretana process.

| | |
|---|---|
| Evaporation | 6 t/hr |
| Purge stream | 9 t/hr |
| Mist eliminator wash | 1.2 t/hr |

The Amagasaki plant has been operated well, reducing $SO_2$ emissions from 800 to below 10 ppm. It has been found that keeping the oxidation in the scrubber below 20 percent helps prevent scaling.

### Evaluation

The process is similar to the Babcock-Hitachi and Mitsubishi-JECCO processes except for the use of the Moretana scrubber. The scrubber is highly effective for $SO_2$ removal but causes much mist and a large pressure drop. The Amagasaki plant has been used also for tests of simultaneous removal of $SO_2$ and $NO_2$ by sodium scrubbing, and therefore has not been operated continuously for a long period with lime scrubbing. Operation of commercial plants, which started recently, should allow further evaluation.

## OTHER WET LIME/LIMESTONE PROCESSES

### IHI-TCA Process

Ishikawajima-Harima Heavy Industires Ltd. (IHI) has constructed two units at the Kumagaya plant, Chichibu Cement Co., each with a capacity of treating 104,000 $Nm^3$/hr of flue gas from diesel engines.[3] Flue gas is first cooled to below 80°C by a cooler, introduced into two TCA absorbers in series, and reacted with milk of lime. The product calcium sulfite is oxidized by air into gypsum after pH adjustment. A low slurry concentration (2 percent) is used to reduce erosion of the plastic balls.

IHI has started construction of another unit for Shikoku-Sumitomo Joint Thermal Power with a capacity of treating 450,000 $Nm^3$/hr of flue gas from an oil-fired boiler containing 1300 ppm $SO_2$ and 0.1 $g/Nm^3$ dust. The unit will be completed by January 1976. About 90 percent of the $SO_2$

and 50 percent of the dust will be removed by a limestone slurry. Tests on balls of different materials are under way.

## Chemico-IHI Process

IHI has started building two units, each with a capacity of treating 900,000 $Nm^3$/hr of flue gas from a coal-fired utility boiler (265 MW), at Isogo Station, Electric Power Development Co., using Chemico scrubbers (Figure 3-25). The flue gas passing through an electrostatic precipitator will be introduced into two Chemico venturi scrubbers in series. A limestone slurry will be fed to the second scrubber and then countercurrently to the first scrubber. The calcium sulfite sludge from the first scrubber will be oxidized by air after pH adjustment with sulfuric acid. The first unit is to be completed by early 1976 and the second in late 1976.

Isogo Station is now burning a low-sulfur coal (0.3 percent S) and will burn a coal with 0.6 percent sulfur after completion of the desulfurization units. Limestone will be ground to pass 325 mesh 95 percent. About 80 percent of the $SO_2$ will be removed. The method of gypsum disposal has not been decided. Although the flue gas will be first passed through an electrostatic precipitator, the scrubber inlet gas will contain a considerable amount of fly ash with relatively low concentrations of $SO_2$; the product gypsum will contain much fly ash and may not be suitable for cement or wallboard manufacture.

## Kawasaki Lime-Magnesium Process

Kawasaki Heavy Industries originally constructed a wet-lime process plant for Jujo Paper Co. (Akita plant, 84,000 $Nm^3$/hr) in 1973 using a multi-venturi type of low-pressure-drop scrubber, which suffered from scaling. Kawasaki later found that addition of magnesium helped prevent scaling and went on to develop a lime-magnesium process. Flue gas is

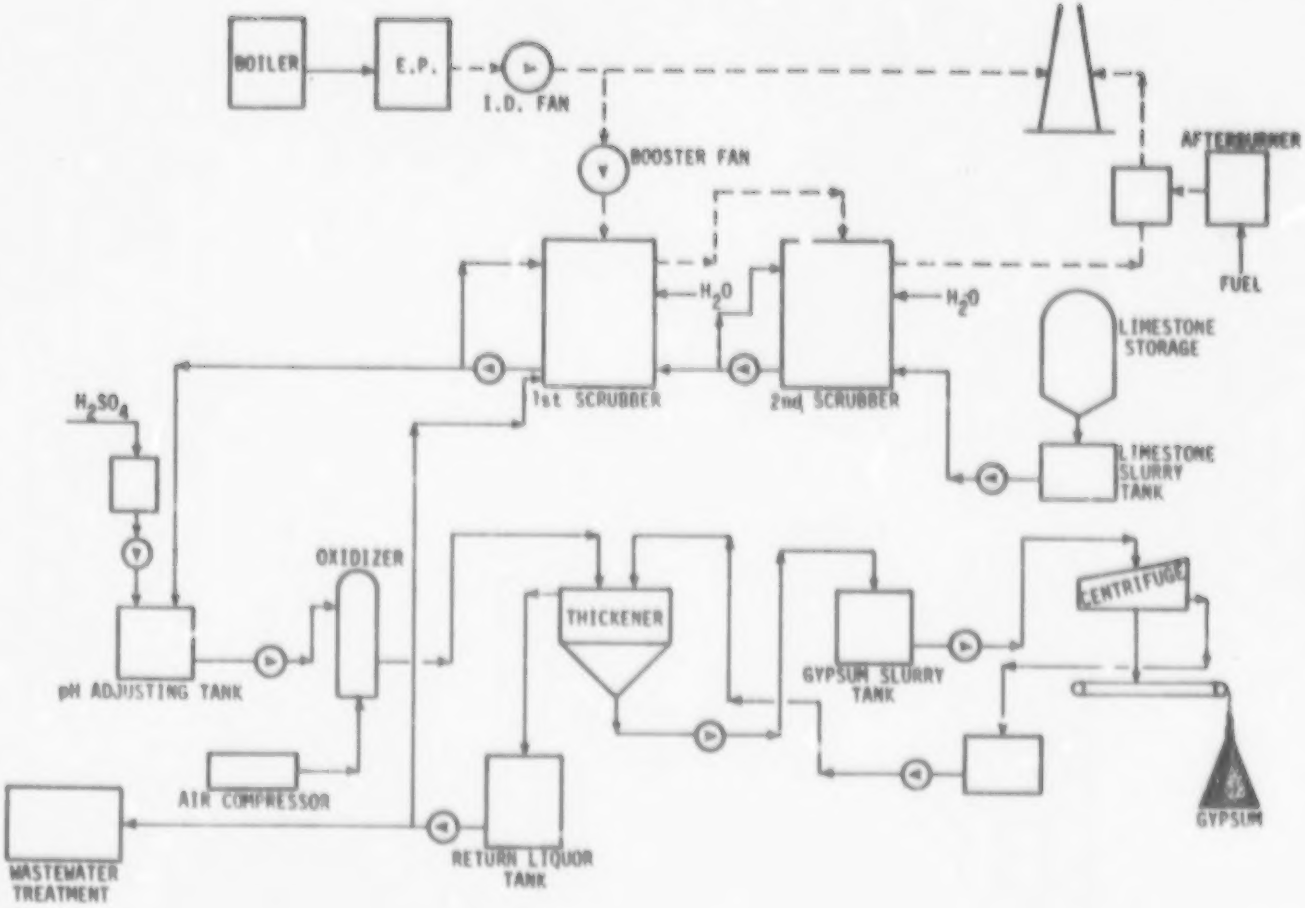

BOILER
E.P.
I.D. FAN
BOOSTER FAN
AFTERBURNER
FUEL
$H_2O$
$H_2O$
1st SCRUBBER
2nd SCRUBBER
LIMESTONE STORAGE
LIMESTONE SLURRY TANK
$H_2SO_4$
OXIDIZER
pH ADJUSTING TANK
THICKENER
GYPSUM SLURRY TANK
CENTRIFUGE
GYPSUM
AIR COMPRESSOR
RETURN LIQUOR TANK
WASTEWATER TREATMENT

Figure 3-25. Flowsheet of Chemico-IHI process (Isogo plant, EPDC).

first cooled and then treated with a mixed slurry of calcium and magnesium hydroxides and gypsum. The reaction product--calcium and magnesium sulfites and gypsum--is oxidized by air after pH adjustment with sulfuric acid. The oxidation forms magnesium sulfate solution and gypsum, which are separated by means of a thickener and a centrifuge. The magnesium sulfate solution (about 5 percent) is sent to a reactor in which lime is added with make-up magnesium hydroxide to precipitate magnesium hydroxide and gypsum, which are sent to the absorber.

Two commercial plants are under construction--one for the Saidaiji plant, Nippon Exlan, and the other for the Okazaki plant, Unitika. Both will have a capacity of treating about 250,000 $Nm^3$/hr of flue gas from an industrial boiler and will be completed by the end of 1975. Limestone will be used in place of lime in one of the plants. More than 90 percent of the $SO_2$ will be removed by using a stoichiometric amount of lime or 1.1 to 1.2 stoichiometric limestone. The gypsum does not grow very well and contains about 0.5 percent magnesium sulfate but is useful as retarder of cement setting.

### Tsukishima Process (TSK Process)

Tsukishima Kikai Co. (TSK) constructed a wet-lime process plant (20 MW equivalent) using Bahco scrubbers at Nagoya plant, Yahagi Iron Co., in 1972.[3] The process is similar to other Japanese processes. There is no plan to build other plants.

### Nippon Kokan Process

Nippon Kokan has operated since 1964 a wet-lime process plant (at Koyasu), treating tail gas from a sulfuric acid plant. The system was constructed by Mitsubishi Heavy Industries using the Mitsubishi-JECCO process. Based on the experience, Nippon Kokan developed its own wet-lime process, which is similar to the Mitsubishi-JECCO process except for the use of a spray tower type absorber. A commercial plant for Nippon Sheet Glass Co. (Yokkaichi plant, 120,000 $Nm^3$/hr) is under construction.

## 4. INDIRECT LIME-LIMESTONE PROCESS (DOUBLE-ALKALI TYPE)

### INTRODUCTION

Many double-alkali-type processes that use lime or limestone as a precipitant have been developed in Japan, including those that use an acidic solution or acid as the absorbent. The Hitachi-Tokyo Electric process uses activated carbon as the absorbent and limestone as the precipitant. All of those processes are classified in the category of "indirect lime-limestone process". Installations with capacities greater than 20 MW equivalent are listed in Table 4-1. The operation parameters are shown in Table 3-2.

### Wet Process

The various processes use different absorbents; a sodium sulfite solution is used for the Showa Denko, Kureha-Kawasaki, and Tsukishima processes; an ammonium sulfite solution for the NKK process; an acidic ammonium sulfate solution for the Kurabo process; an aluminum sulfate solution for the Kowa process; and a dilute sulfuric acid with iron sulfate for the Chiyoda process. The pH values of the solutions are maintained at 6 to 7 for ammonium and sodium sulfites, 3 to 4 for ammonium and aluminum sulfates, and 1 for sulfuric acid. The L/G ratios are 1 to 2 (7 to 14 gal./1000 scf) for the solutions of pH 6 to 7, 3 to 10 for solutions of pH 3 to 4, and 30 to 50 for the acid at pH 1. The more acidic the solution, the lower the $SO_2$ absorption capacity, the lesser the problem of scaling, and the easier the reaction with limestone. Limestone can be reacted with a sodium bisulfite solution, as in the Showa Denko and Kureha-Kawasaki processes, but the reaction occurs slowly

## Table 4-1. INDIRECT LIME-LIMESTONE PROCESSES

(double alkali)

| Process developer | Absorbent precipitant | User | Plant site | MW[a] | Type of plant | Year of completion | Gypsum, tons/day |
|---|---|---|---|---|---|---|---|
| Nippon Kokan | $(NH_4)_2SO_3$, $Ca(OH)_2$ | Nippon Kokan | Keihin | 46 | Sintering plant | 1972 | 15 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Fuji Kosan | Kainan | 50 | Industrial boiler | 1972 | 21 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Mitsubishi Rayon | Otake | 27 | Industrial boiler | 1973 | 21 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Daicel | Aboshi | 31 | Industrial boiler | 1973 | 23 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Mitsubishi Chem. | Yokkaichi | 130 | Industrial boiler | 1974 | 60 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Mitsubishi Pet. Chem. | Yokkaichi | 230 | Industrial boiler | 1974 | 35 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Hokuriku Electric | Toyama | 250 | Utility boiler | 1974 | 180 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Hokuriku Electric | Fukui | 350 | Utility boiler | 1975 | 290 |
| Chiyoda | dil. $H_2SO_4$, $CaCO_3$ | Denki Kagaku | Chiba | 37 | Industrial boiler | 1975 | 35 |
| Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Tohoku Electric | Shinsendai | 150 | Utility boiler | 1974 | 40 |
| Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Shikoku Electric | Shintokushima | 450 | Utility boiler | 1975 | 300 |
| Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Shikoku Electric | Sakaide | 450 | Utility boiler | 1975 | 300 |
| Showa Denko | $Na_2SO_3$, $CaCO_3$ | Showa Denko | Chiba | 150 | Industrial boiler | 1973 | 110 |
| Showa Denko | $Na_2SO_3$, $CaCO_3$ | Showa Pet. Chem. | Kawasaki | 62 | Industrial boiler | 1974 | 70 |
| Showa Denko | $Na_2SO_3$, $CaCO_3$ | Kanegafuchi Chem. | Takasago | 93 | Industrial boiler | 1974 | 80 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Nippon Mining | Saganoseki | 37 | $H_2SO_4$ plant | 1973 | $CaSO_3$ |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Yokohama Rubber | Hiratsuka | 27 | Industrial boiler | 1974 | 20 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Nisshin Oil | Isogo | 27 | Industrial boiler | 1974 | 30 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Poly Plastic | Fuji | 65 | Industrial boiler | 1974 | 70 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Kyowa Pet. Chem. | Yokkaichi | 46 | Industrial boiler | 1974 | 35 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Toho Zinc | Annaka | 43 | $H_2SO_4$ plant | 1974 | 70 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Ajinomoto | Yokkaichi | 25 | Industrial boiler | 1974 | 25 |
| Tsukishima | $Na_2SO_3$, $Ca(OH)_2$ | Kinuura Utility | Nagoya | 63 | Industrial boiler | 1974 | 40 |
| Tsukishima | $Na_2SO_3$, $Ca(OH)_2$ | Daishowa Paper | Fuji | 85 | Industrial boiler | 1975 | 45 |
| Kurabo Engineering | $(NH)_2SO_4$, $Ca(OH)_2$ | Kuraray | Tamashima | 31 | Industrial boiler | 1974 | 30 |
| Kurabo Engineering | $(NH_4)_2SO_4$, $Ca(OH)$ | Daicel | Aboshi | 53 | Industrial boiler | 1975 | 40 |
| Dowa Mining | $Al_2(SO_4)_3$, $CaCO_3$ | Dowa Mining | Okayama | 82 | $H_2SO_4$ plant | 1974 | 24 |
| Hitachi-Tokyo | Carbon, $CaCO_3$ | Tokyo Electric | Kashima | 150 | Utility boiler | 1972 | 50 |

[a] Actual for boilers and equivalent gas flow for other plants. Boilers are oil-fired.

and requires large reaction vessels. Lime is used for the Tsukishima, NKK, and Kurabo processes.

For the Chiyoda, Dowa, and Kurabo processes, the $SO_2$ absorbents are contacted with air to oxidixe sulfite to sulfate. Limestone or lime is then added to precipitate gypsum. For other processes, limestone or lime is added first to precipitate calcium sulfite, which is then oxidized into gypsum. Gypsum crystals produced in the double alkali type process, are usually larger than those produced in the wet lime-limestone process. Moisture content of the by-product gypsum after centrifugation ranges from 6 to 12 percent as compared with 8 to 15 percent for the wet lime-limestone process.

The liquor from the gypsum centrifuge is returned mainly to the scrubber system. Softening of the liquor, which is usally needed to prevent scaling, is not necessary when an acidic solution at a pH below 4 is used.

At most plants, a small portion of the liquor is purged to maintain concentrations of chloride, magnesium, and other impurities under a certain level. Calcium sulfite obtained by the slow reaction of limestone and sodium bisulfite grows into fairly large crystals, which are not difficult to handle. On the other hand, lime reacts rapidly with a sodium bisulfite solution to give very fine crystals of calcium sulfite like those produced by the wet lime-limestone process.

## Carbon Absorption

Another type of indirect lime-limestone process is dry activated carbon absorption, which is used in the Hitachi-Tokyo Electric process. The carbon that has absorbed $SO_2$ is washed with water to give a dilute sulfuric acid of 15 to 20 percent concentration. The acid is treated with powdered limestone to produce gypsum, which is centrifuged to 10 to 12 percent moisture. The process requires large absorption towers because gas velocity is kept low (0.5 m/sec) to obtain 80 to 90 percent removal of the $SO_2$. Hitachi has recently operated a 3000 $Nm^3$/hr pilot plant in which $SO_2$ is absorbed with a carbon slurry. The resulting sulfuric acid is treated with limestone to obtain gypsum.

## SHOWA DENKO SODIUM-LIMESTONE PROCESS

### State of Development

Showa Denko K. K., one of the largest chemical companies in Japan, has developed a sodium-limestone process. About 10 commercial plants have been constructed by Showa Denko and Ebara Manufacturing Co. a licensee of the process (Table 4-1).

### Process Description

Figure 4-1 shows a flowsheet of the Chiba plant, Showa Denko, with a capacity of treating 500,000 $Nm^3$/hr of flue gas from oil-fired boilers (two 75-MW boilers) containing 1200 to 1500 ppm $SO_2$ and 4 to 5 percent $O_2$. The flue gas at 160°C is introduced into four vertical-cone type scrubbers arranged in parallel, washed with a sodium sulfite-bisulfite solution at a pH of about 7, passed through a mist eliminator, reheated by afterburning, and led to a stack. The absorbent liquid is charged from the bottom of the scrubbers, blown up by the gas, and flows back to the liquor inlet by gravity (Figure 4-2). Very good contact between gas and liquid particles ensures about 95 percent removal of $SO_2$ and 80 percent removal of dust at L/G 1.1 (about 8 gallons/1000 scf). The liquor discharged from the scrubber has an $Na_2SO_3/NaHSO_3$ mole ratio of about 1.4. Most of the liquor is recycled to the scrubbers. A portion of the liquor is led to two reactors in series and treated with powdered limestone.

$$2NaHSO_3 + CaCO_3 = Na_2SO_3 + CaSO_3 + H_2O + CO_2$$

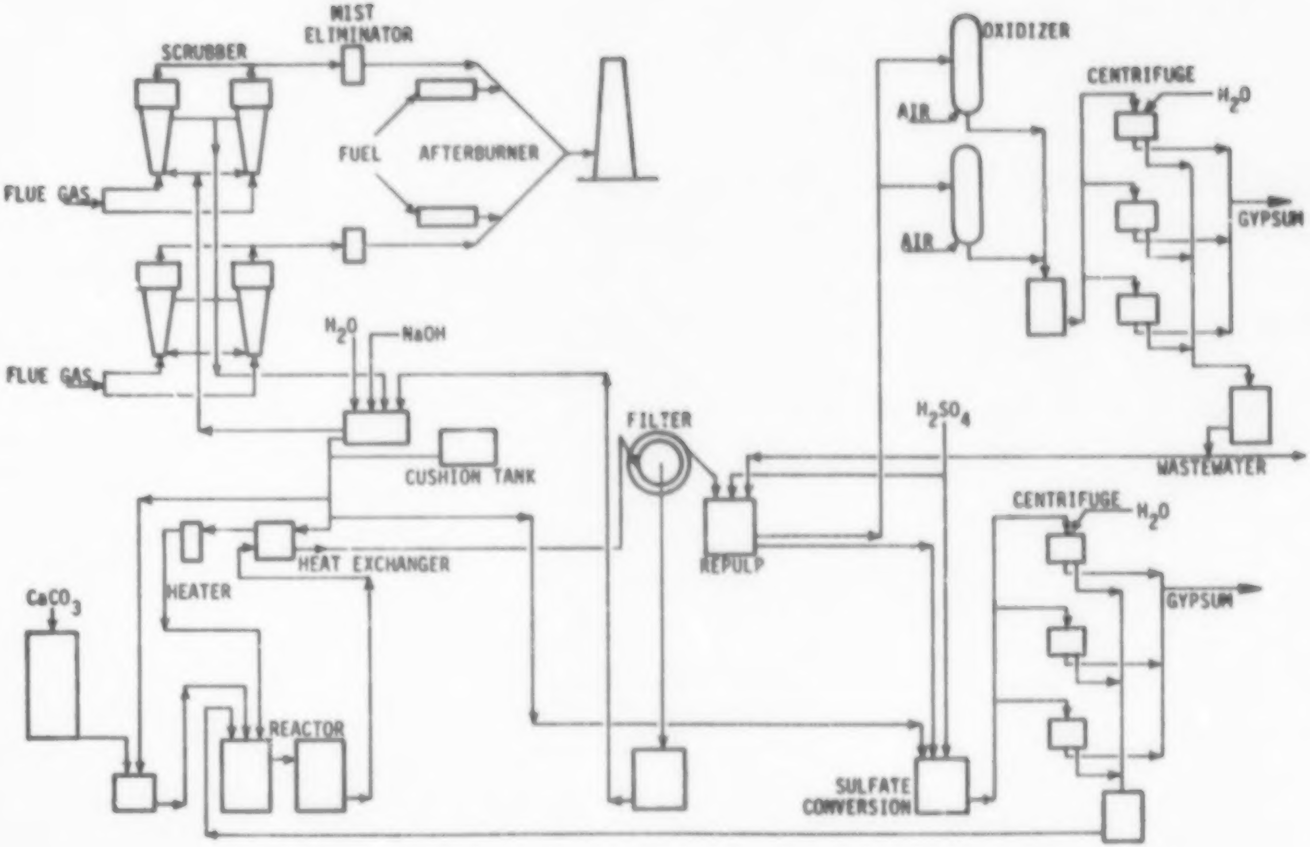

SCRUBBER
MIST ELIMINATOR
FLUE GAS
FLUE GAS
FUEL
AFTERBURNER
$H_2O$
NaOH
CUSHION TANK
HEATER
HEAT EXCHANGER
$CaCO_3$
REACTOR
FILTER
REPULP
$H_2SO_4$
SULFATE CONVERSION
OXIDIZER
AIR
AIR
CENTRIFUGE
$H_2O$
GYPSUM
WASTEWATER
CENTRIFUGE
$H_2O$
GYPSUM

Figure 4-1. Flowsheet of Showa Denko process (Chiba plant, 500,000 $Nm^3/hr$).

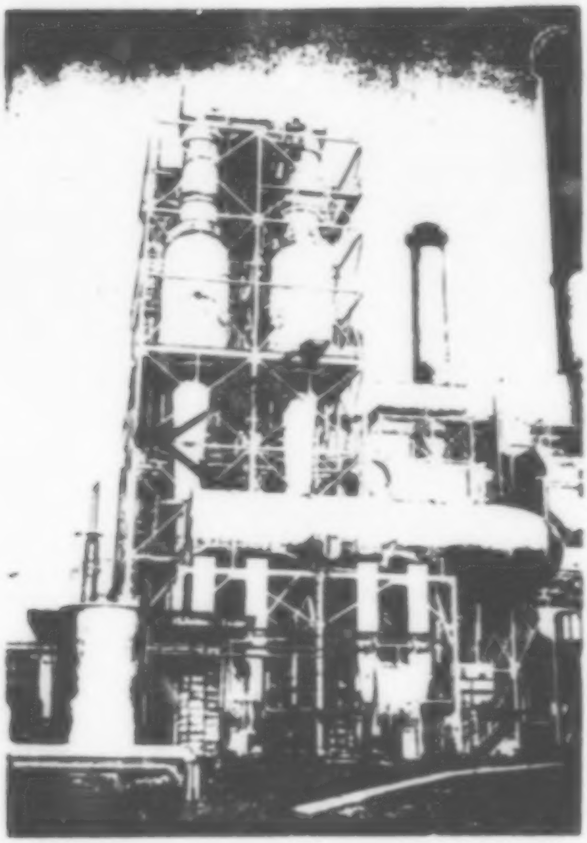


Figure 4-2. Scrubbers (Chiba plant).

Figure 4-3. By-product gypsum (Chiba plant).

The calcium sulfite is separated from the sodium sulfate solution by filtration; the solution is returned to the scrubber. Calcium sulfite is reslurried and oxidized in an oxidizer to form gypsum. As sodium sulfate gradually forms in the solution and tends to accumulate, a portion of the liquor discharged from the scrubber is sent to a sulfate conversion step to maintain the sulfate concentration at a certain level. In the conversion step, the sulfate is treated with calcium sulfite and sulfuric acid to produce gypsum and sodium bisulfite (Figure 4-3).

$$Na_2SO_4 + 2CaSO_3 + H_2SO_4 + 4H_2O = 2(CaSO_4 \cdot 2H_2O) + 2NaHSO_3$$

The bisulfite solution is led to the reactor.

## Status of Technology and Plant Operation

Since start-up of the Chiba plant in January 1973, no problems have occurred with the scrubbing system but occasional problems have occurred with the limestone reaction system. Whenever trouble occurs, fuel is changed to a low-sulfur oil containing about 1 percent sulfur, the flue gas is kept treated by the scrubbers, and some of the sodium sulfite solution is stored in a tank until the trouble is over and the whole system resumes operation. The availability of the whole system from July 1973 to October 1974 is shown in Figure 4-4.

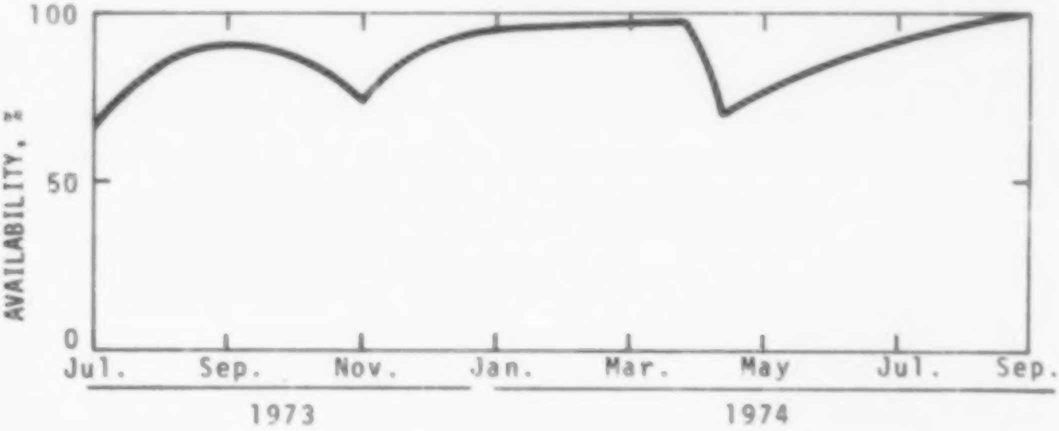


Figure 4-4. Availability of Chiba plant since 1973.

The reaction of limestone and sodium bisulfite is carried out at 90°C for 2 hours. This reaction is delayed by the presence of much magnesium ion in the liquor. Therefore, a portion of the liquor is purged from the system to prevent the accumulation of magnesium ion derived from limestone. The amount of wastewater is about one-half that of gypsum, which reaches about 130 t/day. The gypsum, containing about 9 percent water and less than 300 ppm Na, has been sold for wallboard. The sodium sulfate is decomposed at 60°C at 90 minutes retention time. Some of the operation paramters are as follows:

| | |
|---|---|
| Percent oxidation in the system | 7-8.5 of absorbed $SO_2$ |
| Pressure drop in scrubber | 250 mm $H_2O$ |
| Power requirement | 110 kWh/kl oil or 2.2 percent of generated power |
| Capital cost (late 1973) | $43 (¥13,000)/kW |
| Desulfurization cost since start-up | 4 mills/kWh |

Evaluation

The scrubber is very effective for the removal of both $SO_2$ and dust. High $SO_2$ removal efficiency is attained, by-producing gypsum using limestone. The scrubber operation can be continued even when other process equipment is undergoing repairs. Consumption of sodium hydroxide is low.

Among its disadvantages, the process is more complex than the wet lime-limestone process. The capacity of a scrubber is limited. Use of sulfuric acid is undesirable for plants whose by-product calcium sulfite or gypsum must be discarded.

## KUREHA-KAWASAKI SODIUM-LIMESTONE PROCESS

### State of Development

Kureha Chemical Industry Co. jointly with Kawasaki Heavy Industries has developed a sodium-limestone double-alkali process. The first commercial plant was constructed by Kawasaki at Shinsendai Station, Tohoku Electric Power. Four plants are under construction or being designed (Table 4-2).

Table 4-2. PLANTS USING THE KUREHA-KAWASAKI PROCESS
(All for oil-fired boilers)

| User | Plant site | Capacity, MW | Inlet $SO_2$, ppm | Date of completion |
|---|---|---|---|---|
| Tohoku Electric | Shinsendai | 150 | 600-800 | Jan. 1974 |
| Shikoku Electric | Shintokushima | 450 | 1,000 | Sept. 1975 |
| Shikoku Electric | Sakaide | 450 | 1,000 | Oct. 1975 |
| Confidential | | 350 | 1,000-1,300 | Aug. 1976 |
| Kyushu Electric | Buzen | 250x2 | (1,000-1,300) | Dec. 1976 |

### Process Description

A flowsheet of the Shinsendai plant is shown in Figure 4-5, and plant facilities in Figure 4-6. About one-fourth of the flue gas from a 600-MW oil-fired boiler, passed through an electrostatic precipitator by a forced-draft fan, is fed into a venturi-type precooler and then into a packed-grid-type scrubber, where the gas is washed with a sodium sulfite solution (about 20 percent) at pH 7.0 and a L/G ratio of nearly 2 liters/$Nm^3$ (about 12 gal./1000 scf). The gas is then passed through a mist eliminator, reheated by an afterburner, and led into a stack.

The liquor discharged from the scrubber at pH 6.5 is first filtered to remove carbon dust and then passed through a series of five reactors, where powdered limestone, ground in a vertical tower mill to pass 325 mesh, is reacted to precipitate calcium sulfite and regenerate sodium sulfite.

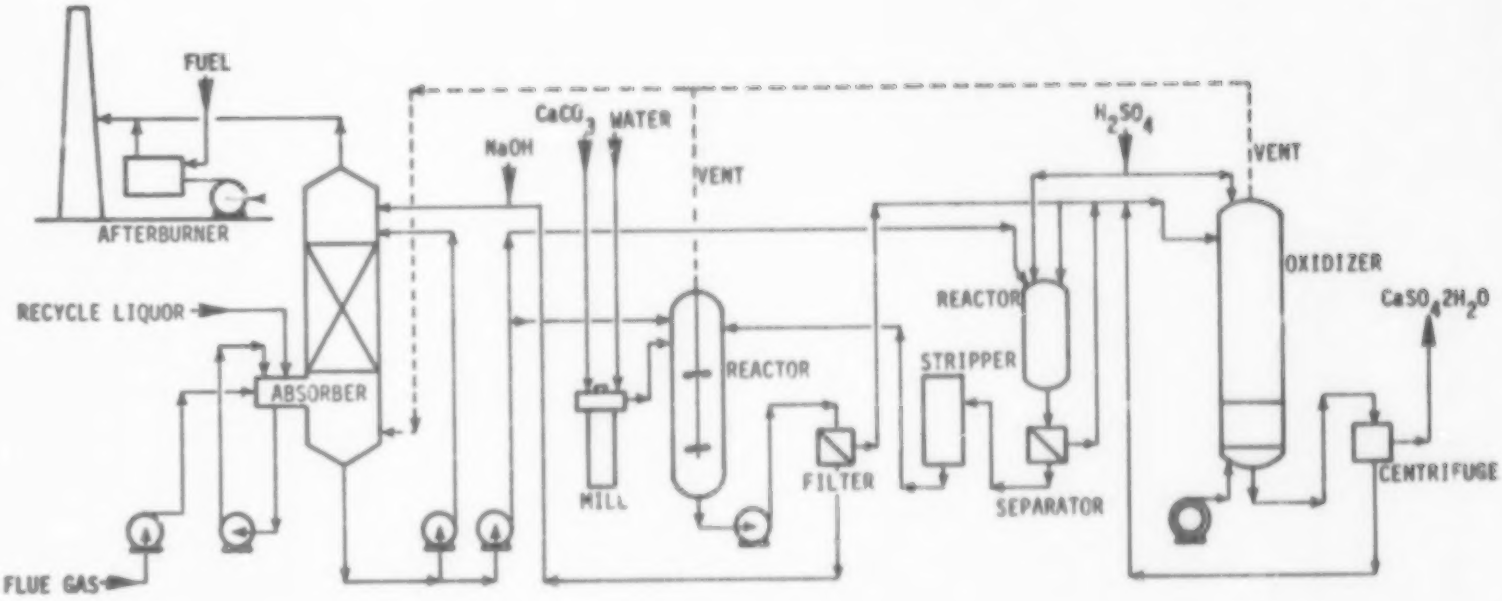
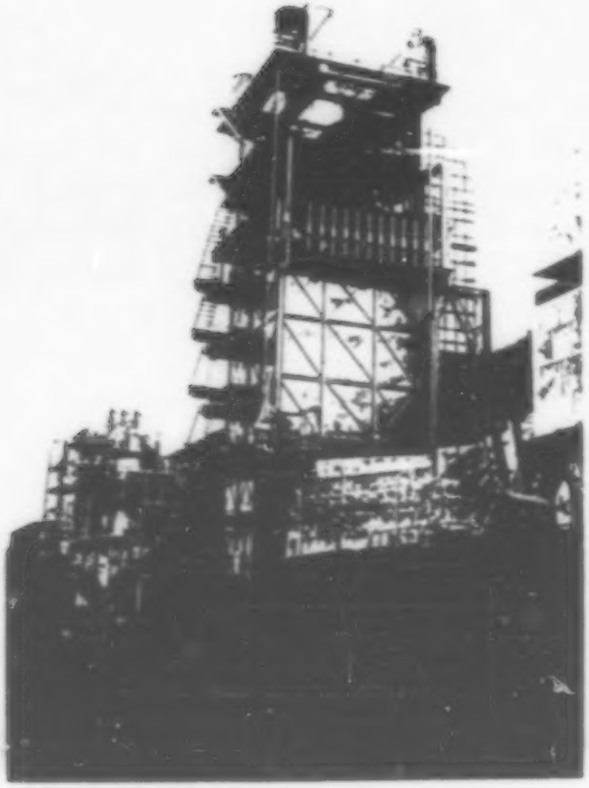

FUEL
AFTERBURNER
RECYCLE LIQUOR
ABSORBER
FLUE GAS
NaOH
$CaCO_3$
WATER
VENT
MILL
REACTOR
FILTER
$H_2SO_4$
VENT
REACTOR
STRIPPER
SEPARATOR
OXIDIZER
$CaSO_4 2H_2O$
CENTRIFUGE

Figure 4-5. Flowsheet of Kureha-Kawasaki process.



Absorber

Reactors and oxidizer

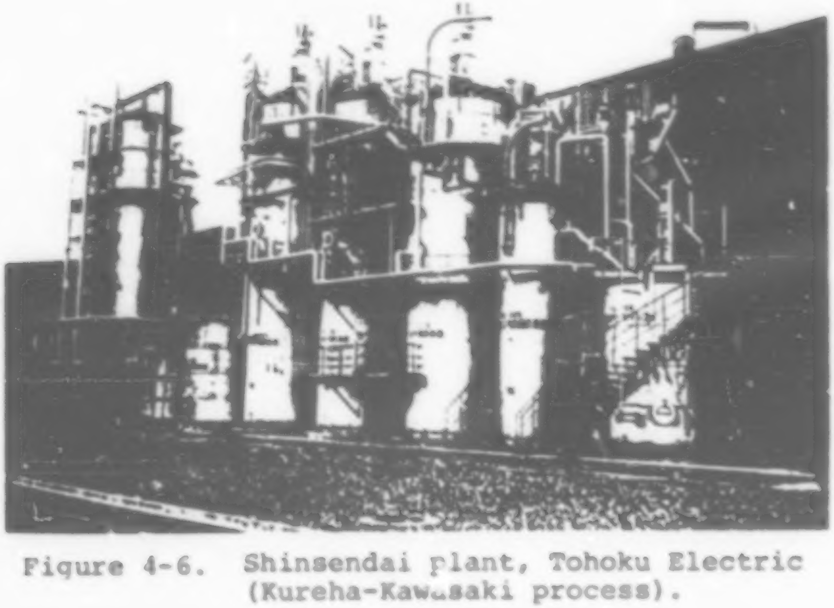


Figure 4-6. Shinsendai plant, Tohoku Electric (Kureha-Kawasaki process).

$$2NaHSO_3 + CaCO_3 = Na_2SO_3 + CO_2 + H_2O$$

A stoichiometric amount of limestone is used and more than 90 percent is reacted in the reactors heated with steam. The pH of the slurry at the outlet is 7.3. The calcium sulfite (50 percent slurry) is separated on a vacuum filter and washed to remove sodium sulfite. The filter cake (about 60 percent water) is repulped to 10 percent slurry, treated with sulfuric acid to reduce the pH, and oxidized by air bubbles in an oxidizer (at 2 atmospheric pressure) developed by Kureha and Kawasaki. The gypsum slurry is centrifuged to less than 8 percent moisture; the separated liquid is recycled to repulp the calcium sulfite.

A portion of the sodium sulfite is oxidized into sulfate in the scrubber by oxygen in the flue gas. A side stream of liquor from the scrubber is treated to decompose the sulfate by reaction with sulfuric acid and calcium sulfite.

$$Na_2SO_4 + 2CaSO_3 + H_2SO_4 + 4H_2O = 2(CaSO_4 \cdot 2H_2O) + 2NaHSO_3$$

The slurry from the desulfation unit is filtered, and the gypsum is sent to the oxidizer for use as a seed to optimize crystal growth; the separated sodium bisulfite solution is heated and stripped to generate $SO_2$. The solution is recycled to the desulfation unit to reduce sulfuric acid consumption.

## Performance

The Shinsendai plant has been operated smoothly since its start-up in January 1974. Inlet $SO_2$ concentrations range from 600 to 800 ppm and outlet concentrations are lower than 10 ppm. The pressure drop in the scrubber and mist eliminator is 200 mm $H_2O$. There have been no scaling or plugging problems. Even if scale forms, it will not accumulate to an appreciable thickness for several years because the concentration of calcium ion in the circulating liquor is less than 10 ppm.

About 20 tons/hr of water are charged to the system and the same amount is removed by volatilization, as water of crystallization, and as moisture of gypsum. No wastewater has been emitted so far. Because magnesium derived from limestone accumulates in the liquor and interferes with the reaction of limestone and sodium bisulfite, a water treatment unit to remove magnesium has been installed.

The plant can be operated by two persons per shift.

## Evaluation

The $SO_2$ removal efficiency is very high (over 97 percent). Gypsum grows into large crystals and can be centrifuged to a very low moisture content (5 to 6 percent) and thus the loss of sodium is low. Other advantages include the use of limestone and smooth operation. The process, however, is complicated and requires many pieces of equipment. The capital cost was $50/kW in 1973 and may be double that amount in 1974. Moreover, a considerable amount of sulfuric acid is required. Therefore, the process may not be suitable for the U.S., where such high $SO_2$ removal efficiency and good quality of gypsum are not required.

Kawasaki has been testing the electrolysis of sodium sulfate to produce sodium hydroxide and sulfuric acid. If this can be done successfully the desulfurization process step will be eliminated; the side stream from the scrubber will be cooled to crystallize sodium sulfate, which will be separated and subjected to the electrolysis. The by-product sodium hydroxide will be used for make-up and the sulfuric acid for decomposition of the unreacted limestone. Although this process seems sound theoretically, operation of the whole system may be complex.

Although emission of no wastewater is another advantage of the process, some means to remove chloride in the liquor will be required after a long run.

## NIPPON KOKAN AMMONIA SCRUBBING PROCESS

### State of Development

Nippon Kokan, one of the largest steel producers in Japan, has developed an ammonia scrubbing process to combine ammonia in coke-oven gas with $SO_2$ in a waste gas from an iron-ore sintering plant. A prototype plant with a capacity of 150,000 $Nm^3$/hr of waste gas has been operating at Keihin Works in the following two ways: 1) ammonium sulfite formed by the reaction is oxidized to produce ammonium sulfate; 2) ammonium sulfite is treated with lime to precipitate calcium sulfite, which is oxidized by air into gypsum, and to recover ammonia, which is returned to the absorbing system.

Because of the recent world shortage of nitrogen fertilizer, Nippon Kokan has decided to install two large desulfurization units that by-produce ammonium sulfate. One of them, with a capacity of treating 760,000 $Nm^3$/hr of waste gas, will be completed at Fukuyama Works, Nippon Kokan, by the end of 1976; the other, with a capacity of 1,130,000 $Nm^3$/hr, will be completed at Ogishima Works by late 1977. In both plants $SO_2$ in waste gas from iron-ore sintering plants will be combined with ammonia in coke-oven gas.

For the sintering, at present, 95 parts of low-sulfur powdery iron ore (S = 0.03 percent) and 5 parts of coke (S = 0.55 percent) are used, and the waste gas contains about 250 ppm $SO_2$. After the full-scale desulfurization units are installed, cheaper high-sulfur iron ore will be used to give about 400 ppm $SO_2$ in waste gas. The $SO_2$ will be reduced to 30 ppm by scrubbing.

### Process Description

A detailed flowsheet of the prototype plant for the ammonium sulfate process is shown in Figure 4-7. Waste gas issuing from the sintering plant at a rate of 150,000 $Nm^3$/hr at 110 to 130°C contains 250 to 500 ppm $SO_2$, 10 to 12 percent $O_2$, 40 to 60 ppm chloride, and 0.05 g/$Nm^3$ dust. After being passed through an electrostatic precipitator the gas is introduced into a cooler (spray tower) to remove most of

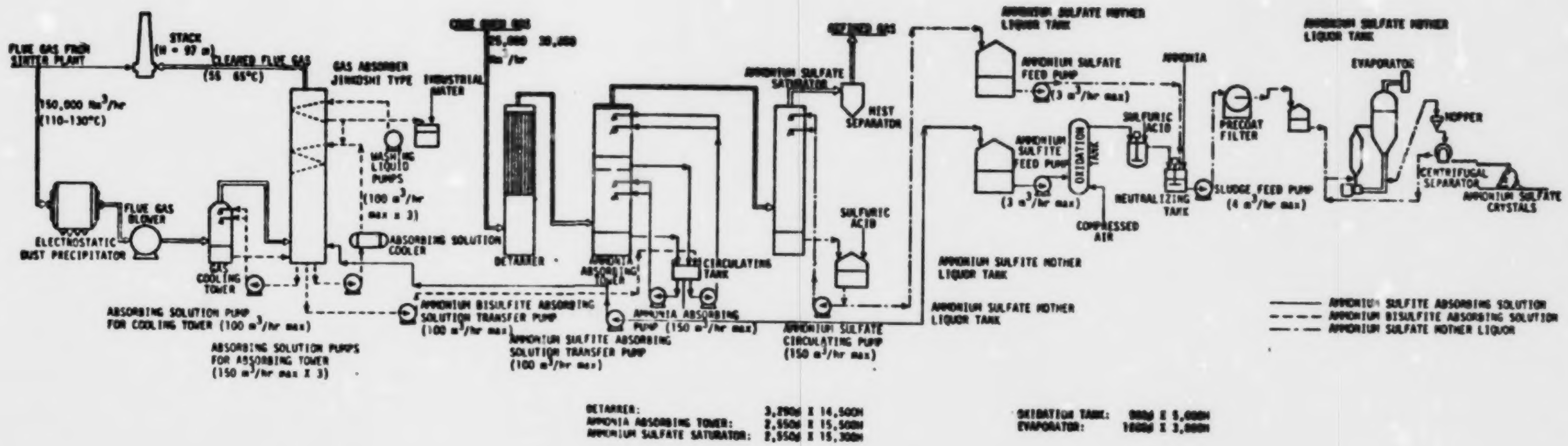

FLUE GAS FROM SINTER PLANT
150,000 Nm³/hr
(110-130°C)
STACK
(H = 97 m)
CLEANED FLUE GAS
(55 65°C)
ELECTROSTATIC DUST PRECIPITATOR
FLUE GAS BLOWER
GAS COOLING TOWER
GAS ABSORBER JINKOSHI TYPE
INDUSTRIAL WATER
WASHING LIQUID PUMPS
(100 m³/hr max x 3)
ABSORBING SOLUTION COOLER
ABSORBING SOLUTION PUMP FOR COOLING TOWER (100 m³/hr max)
ABSORBING SOLUTION PUMPS FOR ABSORBING TOWER (150 m³/hr max X 3)
COKE OVEN GAS
25,000 30,000
Nm³/hr
DETARRER
AMMONIUM BISULFITE ABSORBING SOLUTION TRANSFER PUMP (100 m³/hr max)
AMMONIA ABSORBING TOWER
CIRCULATING TANK
AMMONIA ABSORBING PUMP (150 m³/hr max)
AMMONIUM SULFITE ABSORBING SOLUTION TRANSFER PUMP (100 m³/hr max)
AMMONIUM SULFATE SATURATOR
REFINED GAS
MIST SEPARATOR
SULFURIC ACID
AMMONIUM SULFATE CIRCULATING PUMP (150 m³/hr max)
AMMONIUM SULFITE MOTHER LIQUOR TANK
AMMONIUM SULFATE MOTHER LIQUOR TANK
AMMONIUM SULFATE MOTHER LIQUOR TANK
AMMONIUM SULFATE FEED PUMP
(3 m³/hr max)
AMMONIUM SULFITE FEED PUMP
(3 m³/hr max)
OXIDATION TANK
COMPRESSED AIR
SULFURIC ACID
AMMONIA
NEUTRALIZING TANK
SLUDGE FEED PUMP (4 m³/hr max)
PRECOAT FILTER
AMMONIUM SULFATE MOTHER LIQUOR TANK
EVAPORATOR
HOPPER
CENTRIFUGAL SEPARATOR
AMMONIUM SULFATE CRYSTALS
AMMONIUM SULFITE ABSORBING SOLUTION
AMMONIUM BISULFITE ABSORBING SOLUTION
AMMONIUM SULFATE MOTHER LIQUOR
DETARRER: 3,290φ X 14,500H
AMMONIA ABSORBING TOWER: 2,550φ X 15,500H
AMMONIUM SULFATE SATURATOR: 2,550φ X 15,300H
OXIDATION TANK: 900φ X 5,000H
EVAPORATOR: 1600φ X 3,800H

Figure 4-7. Schematic flowsheet - Nippon Kokan ammonia scrubbing process.

the chloride and dust and then into a Jinkoshi type scrubber (Figure 4-8), in which five stages of screens are placed with some inclination. An ammoniacal solution of about 30 percent concentration flows on the lower three stages forming a liquid film, which absorbs $SO_2$. Water flows on the upper two stages and reduces the plume, which is formed by the ammonia scrubbing of $SO_2$. About 95 percent of the $SO_2$ is removed when the pH of the solution is about 6. Very little ammonia is lost when the pH is 6 or below.

The outlet liquor containing ammonium bisulfite is sent to an ammonia absorber. Coke-oven gas containing a small amount of ammonia is introduced into the absorber. The liquor is sprayed to absorb ammonia and to form an ammonium sulfite solution. A large portion of the solution is returned to the scrubber to absorb $SO_2$. The rest of the solution is sent to an oxidizer, where the sulfite is oxidized into sulfate by air bubbles produced by rotary atomizers. The ammonium sulfate solution is evaporated to produce crystal ammonium sulfate.

For the ammonia-lime process (Figures 4-9 and 4-10), the $SO_2$ absorbing part is the same as in the ammonium sulfate process except that no coke-oven gas is used. A portion of the liquor from the scrubber is sent to a reactor and is reacted with milk of lime (10 percent concentration) under normal pressure at 100°C. The ammonia released here is sent to the ammonia absorber to be absorbed by the liquor from the scrubber. Calcium sulfate and sulfite are precipitated in the reactor. The slurry from the reactor is acidified with sulfuric acid to adjust the pH to 4 to promote oxidation. The slurry is then led into an oxidizer equipped with rotary atomizers to convert calcium sulfite to gypsum, which is then centrifuged. Salable gypsum of good quality is obtained. The gas from the oxidizer contains $SO_2$ and is sent to the scrubber.

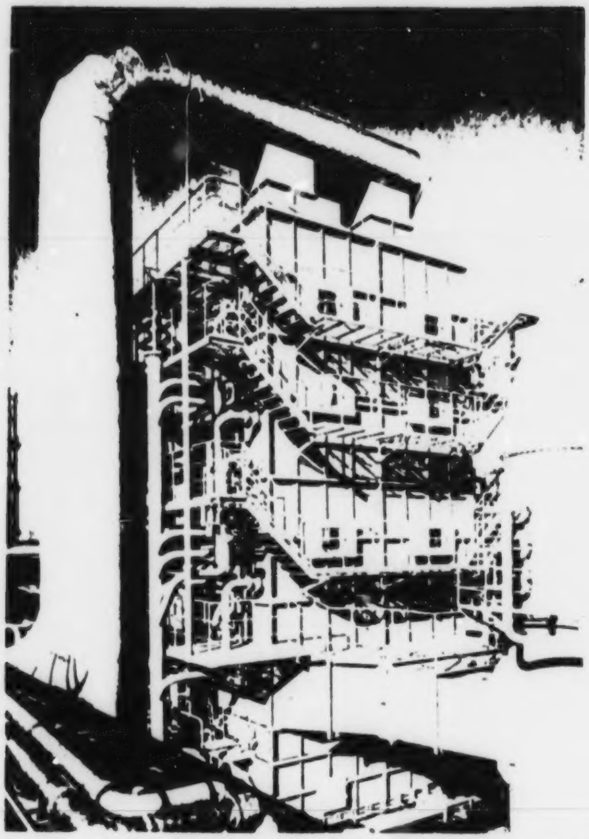


Figure 4-8. Jinkoshi scrubber (Nippon Kokan).

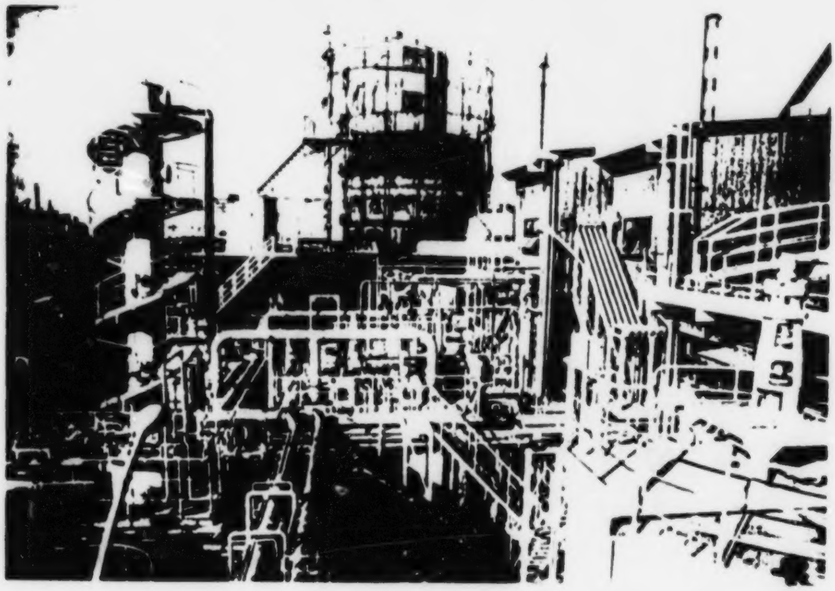


Figure 4-9. Ammonia-lime process (Nippon Kokan).

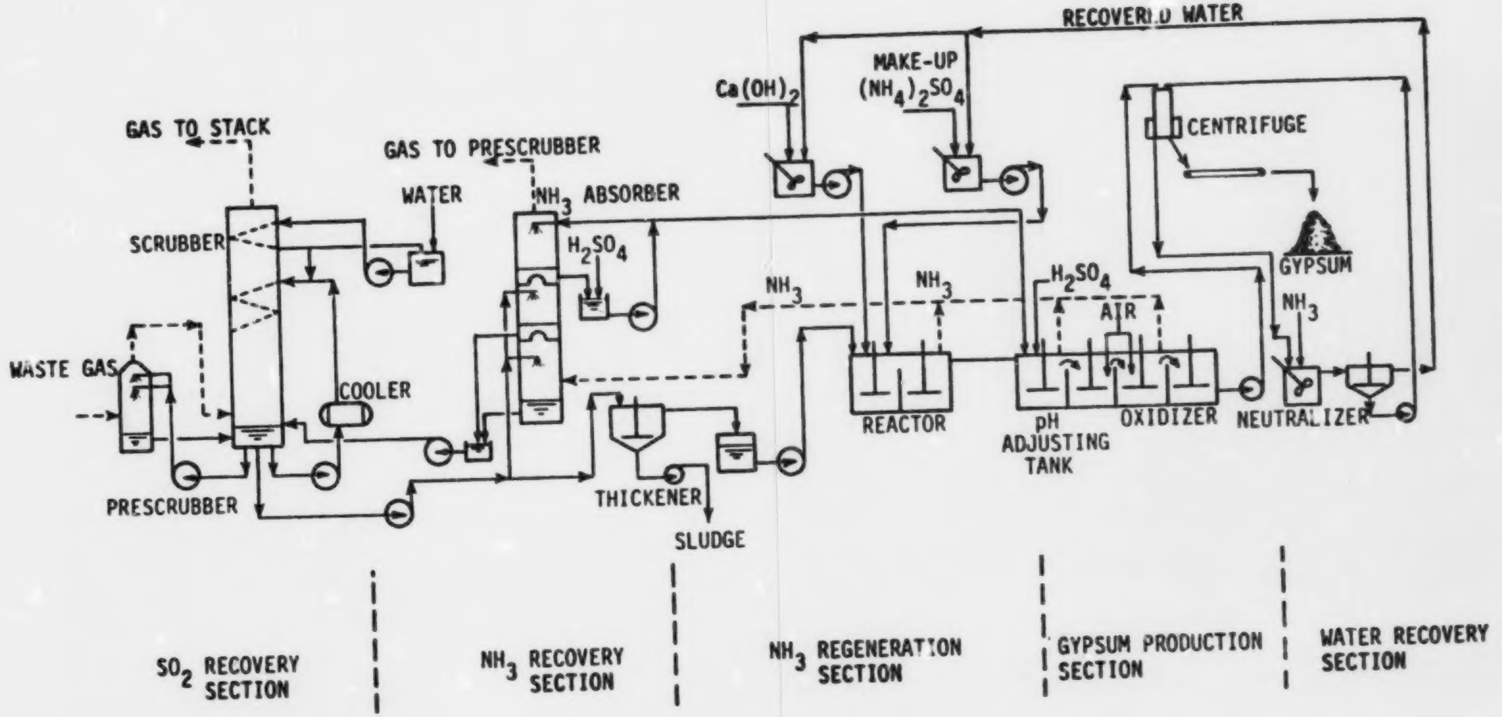

RECOVERED WATER
Ca(OH)$_2$
MAKE-UP
(NH$_4$)$_2$SO$_4$
CENTRIFUGE
GAS TO STACK
GAS TO PRESCRUBBER
WATER
NH$_3$ ABSORBER
SCRUBBER
H$_2$SO$_4$
GYPSUM
NH$_3$
NH$_3$
H$_2$SO$_4$
AIR
NH$_3$
WASTE GAS
COOLER
REACTOR
pH
ADJUSTING
TANK
OXIDIZER
NEUTRALIZER
PRESCRUBBER
THICKENER
SLUDGE
SO$_2$ RECOVERY SECTION
NH$_3$ RECOVERY SECTION
NH$_3$ REGENERATION SECTION
GYPSUM PRODUCTION SECTION
WATER RECOVERY SECTION

Figure 4-10. Nippon Kokan ammonia-lime process.

## Status of Technology

The Jinkoshi type scrubber at the Keihin Works is 19 meters high with a cross section of 4.7 by 7.7 meters. It uses an L/G ratio of about 2 liters/$m^3$; gas velocity is 3 to 4 meters/sec. The pressure drop in the scrubber is about 300 mm $H_2O$.

A model of the scrubber to be used at the Fukuyama Works (760,000 $Nm^3$/hr) is shown in Figure 4-11. In order to maintain a uniform gas flow, fine mesh screens will be placed in parallel to the five-stage screens and about 2 inches above them. The pressure drop in the scrubber will be 350 mm $H_2O$. During a recent operation of the Keihin plant by the ammonia-lime process, the concentration of $SO_2$ was low (about 250 ppm) and that of oxygen high (12 percent). Consequently, extensive oxidation occurred in the scrubber, yielding liquor of the following composition:

| | |
|---|---|
| $(NH_4)_2SO_4$ | 2.0 moles/liter |
| $(NH_4)_2SO_3$ | 0.4 mole/liter |
| $NH_4HSO_3$ | 0.6 mole/liter |
| $(NH_4)_2S_2O_3$ | 0.03 mole/liter |

These composition data show that the oxidation ratio was 70 percent. Tests with a gas containing 700 ppm $SO_2$ showed that the ratio was 50 percent and that $SO_2$ concentration in the scrubber outlet gas was 50 ppm.

When coke-oven gas is used as the source of ammonia, a larger amount of ammonium thiosulfate, $(NH_4)_2S_2O_3$, is formed. As the thiosulfate is hardly oxidized in the oxidizer, it is decomposed by addition of sulfuric acid to the liquor discharged from the oxidizer.

$$(NH_4)_2S_2O_3 + H_2SO_4 = (NH_4)_2SO_4 + S + SO_2 + H_2O$$

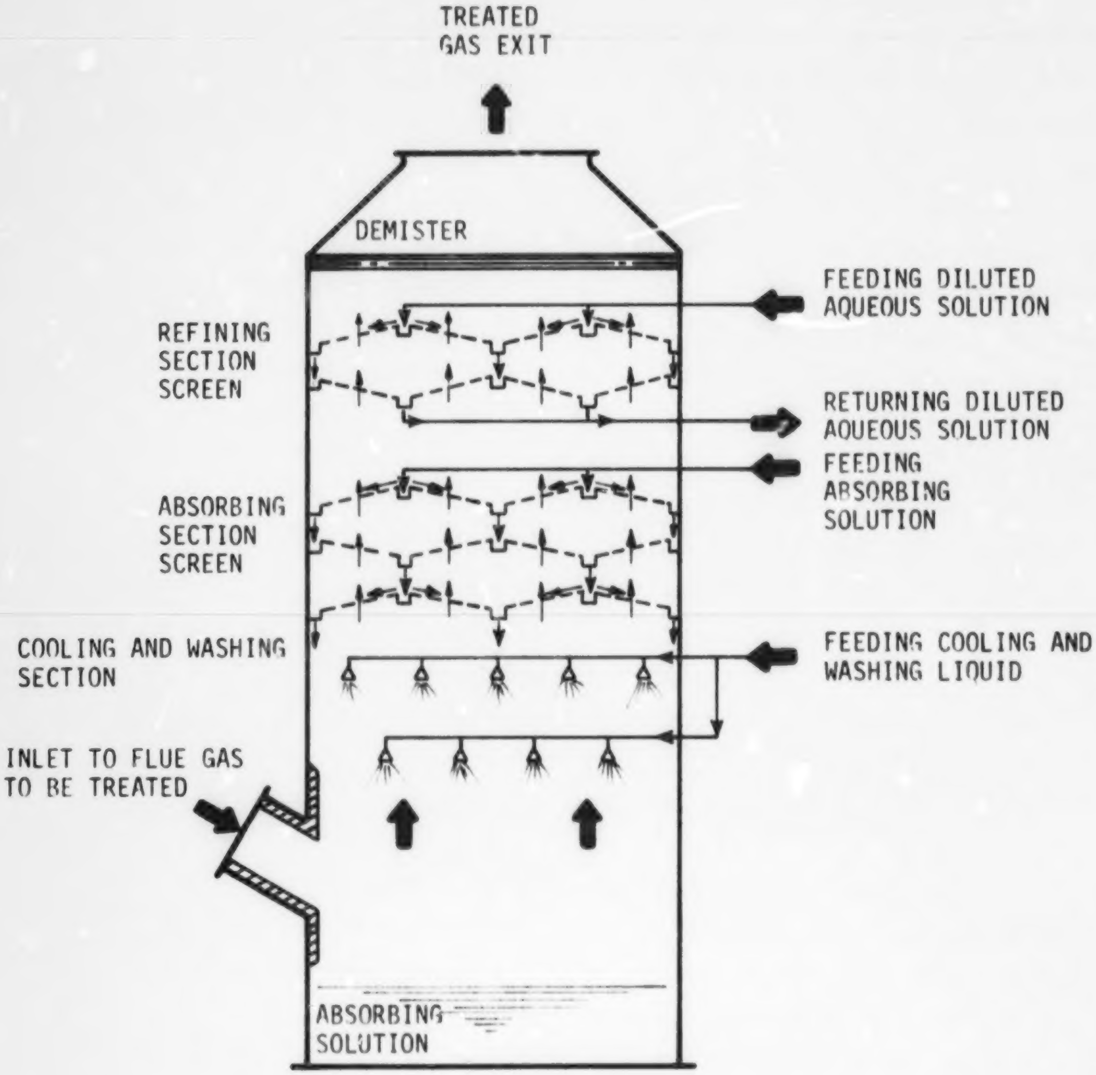

TREATED GAS EXIT
DEMISTER
FEEDING DILUTED AQUEOUS SOLUTION
REFINING SECTION SCREEN
RETURNING DILUTED AQUEOUS SOLUTION
FEEDING ABSORBING SOLUTION
ABSORBING SECTION SCREEN
COOLING AND WASHING SECTION
FEEDING COOLING AND WASHING LIQUID
INLET TO FLUE GAS TO BE TREATED
ABSORBING SOLUTION

Figure 4-11. Jinkoshi-NKK type scrubber.

Plume formation has been a problem because the treated gas has been emitted without reheating. In tests at the Keihin Works with a portion of the gas (3100 $Nm^3/hr$), the plume almost disappeared when the gas was heated to 130°C with an afterburner. An afterburner will be installed at the Fukuyama plant and a wet electrostatic precipitator at the Ogishima plant to allow comparison of the effectiveness of these devices in reducing plume emissions.

## Economics

Table 4-3 lists the annual requirements for operation of plants of different capacities by the ammonium sulfate process using coke-oven gas and by the ammonia-lime process. Estimated costs for both processes are listed in Tables 4-4 and 4-5.

## Table 4-3. ANNUAL REQUIREMENTS FOR OPERATION[a] OF THE NIPPON KOKAN PROCESSES

| | Ammonium sulfate process | | | Ammonia-lime process | | |
|---|---|---|---|---|---|---|
| | 300,000 $Nm^3/hr$ | 500,000 $Nm^3/hr$ | 800,000 $Nm^3/hr$ | 300,000 $Nm^3/hr$ | 500,000 $Nm^3/hr$ | 800,000 $Nm^3/hr$ |
| Ammonia, t | 332 | 498 | 830 | 191 | 315 | 498 |
| Water, 1000 t | 332 | 498 | 830 | 166 | 282 | 448 |
| Steam, t | 14,110 | 20,750 | 34,860 | 27,400 | 47,300 | 71,500 |
| Power, MW-hr | 11,122 | 17,928 | 28,137 | 12,100 | 20,200 | 32,300 |
| $H_2SO_4$, t | 1,577 | 1,826 | 3,362 | 482 | 796 | 1,270 |
| NaOH, t | | | | 69 | 114 | 181 |
| CaO, t | | | | 2,610 | 4,520 | 7,190 |
| Oil, kl | 8,300 | 13,280 | 20,750 | 8,300 | 13,280 | 20,750 |
| By-product t | 6,640 | 9,960 | 16,600 | 6,930 | 11,500 | 18,500 |

[a] The following conditions are assumed: inlet $SO_2$ concentration is 400 ppm, outlet 40 ppm, and the gas is reheated to 130°C.

Table 4-4. ESTIMATED COST OF NKK TYPE AMMONIUM SULFATE SYSTEM (EARLY 1973)

| | 1 | 2 | 3 | Remarks |
|---|---|---|---|---|
| Amount of treated gas, $Nm^3/hr$ | 300,000 | 500,000 | 800,000 | |
| Construction cost [A] (¥ 1000) | 810,000 | 1,100,000 | 1,400,000 | |
| Fixed charges [B] (¥ 1000) | 192,774 | 264,704 | 345,258 | $B = B_1 + B_2 + B_3 + B_4$ |
| Interest, depreciation [$B_1$] | 146,529 | 198,990 | 253,260 | $B_1 = 0.1809 \times A$ |
| Repair [$B_2$] | 24,300 | 33,000 | 42,000 | $B_2 = 0.03 \times A$ |
| Insurance [$B_3$] | 972 | 1,320 | 1,680 | $B_3 = 0.0012 \times A$ |
| Administration [$B_4$] | 20,973 | 31,484 | 48,318 | $B_4 = 0.1 \times B_2 + B_3 + C$ |
| Variable expenses C (¥ 1000) | 184,458 | 280,521 | 439,496 | $C = C_1 + C_2$ |
| Labor [$C_1$] | 12,000 | 12,000 | 12,000 | ¥ 2,000,000 x 6 men/year |
| Secondary materials [$C_2$] | 172,458 | 268,521 | 427,496 | |
| By-product [D] (¥ 1000) | 33,200 | 49,800 | 83,000 | |
| Desulfurization [E] (¥ 1000) | 344,032 | 495,515 | 701,754 | $E = B + C - D$ |
| Unit desulfurization (¥/kl) | 1,650 | 1,420 | 1,250 | |

Table 4-5. ESTIMATED COST OF NKK TYPE AMMONIA-LIME SYSTEM (EARLY 1973)

| | 1 | 2 | 3 | Remarks |
|---|---|---|---|---|
| Amount of treated gas, $Nm^3$/hr | 400,000 | 800,000 | 1,500,000 | |
| Construction cost [A] (¥ 1000) | 850,000 | 1,200,000 | 1,900,000 | |
| Fixed charges [B] (¥ 1000) | 210,370 | 311,909 | 513,916 | $B = B_1 + B_2 + B_3 + B_4$ |
| Interest, depreciation [$B_1$] | 153,765 | 217,080 | 343,710 | $B_1 = 0.1809 \times A$ |
| Repair [$B_2$] | 25,500 | 36,000 | 57,000 | $B_2 = 0.03 \times A$ |
| Insurance [$B_3$] | 1,020 | 1,440 | 2,280 | $B_3 = 0.0012 \times A$ |
| Administration [$B_4$] | 30,085 | 57,389 | 110,926 | $B_4 = 0.1 \times B_2 + B_3 + C$ |
| Variable expenses [C] (¥ 1000) | 274,334 | 536,453 | 1,049,978 | $C = C_1 + C_2$ |
| Labor [$C_1$] | 14,000 | 14,000 | 14,000 | ¥ 2,000,000 x 7 men/year |
| Secondary materials [$C_2$] | 260,334 | 522,453 | 1,035,978 | |
| By-product [D] (¥ 1000) | 69,720 | 139,440 | 277,200 | |
| Desulfurization [E] (¥ 1000) | 414,984 | 708,922 | 1,286,694 | $E = B + C - D$ |
| Unit desulfurization (¥/kl) | 1,488 | 1,271 | 1,230 | |

### Evaluation

The scrubber is effective and capable of treating a large amount of gas, up to 1,500,000 $Nm^3$/hr with one scrubber. In the ammonium sulfate process, both $SO_2$ in waste gas and ammonia in coke-oven gas are utilized. In the ammonia-lime process, salable gypsum of good quality is obtained with no scaling problem.

Negatively, the formation of thiosulfate necessitates additional facilities and the plume problem might not be entirely solved.

## CHIYODA DILUTE SULFURIC ACID PROCESS[7]

### Outline of the Process

Chiyoda Chemical Engineering and Construction Co. has developed a unique process for $SO_2$ recovery. The flue gas is washed with dilute sulfuric acid, which contains an iron catalyst and is saturated with oxygen. $SO_2$ is absorbed and oxidized to sulfuric acid. Part of the acid is reacted with limestone to produce gypsum. The rest is diluted with gypsum wash water and returned to the absorber. Commercial plants using the Chiyoda process are listed in Table 4-6.

### Description

A flow sheet is shown in Figure 4-12. Flue gas is first treated by a prescrubber to eliminate dust and to cool the gas to 55°C. The cooled gas is led into a packed tower absorber containing 2-inch Tellerette. Dilute sulfuric acid (2 to 5 percent $H_2SO_4$), which contains ferric ion as a catalyst and is saturated with oxygen, and fed to the packed tower. About 90 percent of the $SO_2$ is absorbed, and partly oxidized into sulfuric acid.

The product acid is led to the oxidizing tower, into which air is bubbled from the bottom to complete the oxidation. Most of the acid is returned to the absorber at 50 to 60°C, saturated with oxygen. Part of the acid is treated with powdered limestone (74 percent under 200 mesh) to

Table 4-6. COMMERCIAL PLANTS USING THE CHIYODA PROCESS

| Owner of plant | Location | Capacity, $Nm^3/hr$ | Gas source | Completion |
|---|---|---|---|---|
| Nippon Mining Co. | Mizushima | 33,500 | Claus plant | Nov. 1972 |
| Fuji Kosan Co. | Kainan | 157,200 | Boiler & Claus | Nov. 1972 |
| Mitsubishi Rayon Co. | Otake | 90,000 | Boiler | Jan. 1973 |
| Tohoku Oil Co. | Sendai | 14,070 | Claus plant | Feb. 1973 |
| Daicel Co. | Aboshi | 100,000 | Boiler | Nov. 1973 |
| Amagasaki Co. | Kakogawa | 36,200 | Waste gas from waste liquid treatment | Feb. 1974 |
| Hokuriku Elect. Co. | Toyama | 750,000 | Power boiler | May 1974 |
| Mitsubishi Chem. Co. | Yokkaichi | 400,000 | Boiler | May 1974 |
| Mitsubishi Pet. Chem. Co. | Yokkaichi | 150,000 | Boiler | Sept. 1974 |
| Mitsubishi Pet. Chem. Co. | Yokkaichi | 700,000 | Boiler | Sept. 1974 |
| Gulf Power Co. | Florida, U.S.A. | 85,000 | Power boiler | Nov. 1974 |
| Denki Kagaku Co. | Chiba | 120,000 | Boiler | Feb. 1975 |
| Hokuriku Elect. Co. | Fukui | 1,050,000 | Power boiler | May 1975 |
| Toyama Kyodo Elect. Co. | Kusajima | 750,000 | Power boiler | Sept. 1975 |
| Hokuriku Elect. Co. | Toyama | 750,000 | Power boiler | April 1976 |

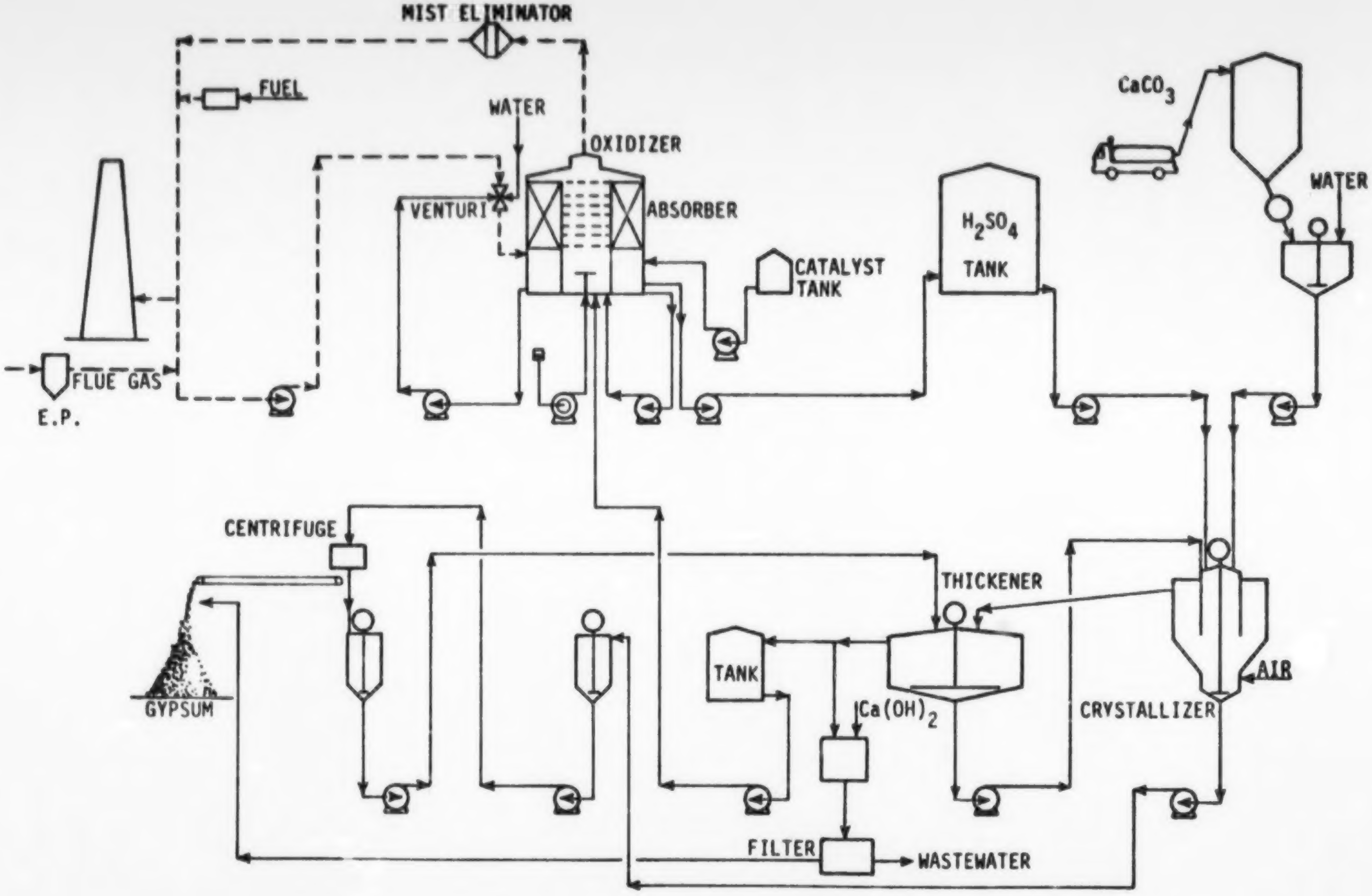

MIST ELIMINATOR
FUEL
WATER
OXIDIZER
VENTURI
ABSORBER
CATALYST TANK
$H_2SO_4$ TANK
$CaCO_3$
WATER
FLUE GAS
E.P.
CENTRIFUGE
THICKENER
TANK
$Ca(OH)_2$
AIR
CRYSTALLIZER
GYPSUM
FILTER
WASTEWATER

Figure 4-12. Flowsheet of Chiyoda process (Toyama plant, Hokuriku Electric).

produce gypsum. A special type of crystallizer has been developed to obtain good crystalline gypsum 100 to 500 microns in size. The gypsum is centrifuged from the mother liquor and washed with water. The product gypsum is of good quality and salable.

The mother liquor and wash water are sent to the scrubber. A small amount of wastewater is discharged to prevent the accumulation of chloride in the circulating liquor because it promotes corrosion.

Status of Technology

The iron catalyst is less reactive at low temperatures but is as reactive as manganese catalyst at operating temperatures above 50°C (Figure 4-13). It is not poisoned by impurities in the gas, even when flue gas from a coal-fired boiler is used. Catalyst loss is very small (Figure 4-14). The towers of commercial plants are provided with rubber or FRP linings. Stainless steel is also usable; ferric catalyst works also as a corrosion inhibitor.

A high L/G ratio is required to attain high $SO_2$ recovery, as shown in Figure 4-15; large pumps and a fairly large absorber and oxidizer are required, as shown in Table 4-7.

Table 4-7. SIZE OF TOWERS REQUIRED FOR THE CHIYODA PROCESS (meters)

| | Absorber | | Oxidizer | |
|---|---|---|---|---|
| Capacity, $Nm^3$/hr | Diameter | Height | Diameter | Height |
| 200,000 | 9.9 | 16.5 | 4.5 | 20.9 |
| 400,000 | 16.5 | 16.5 | 7.0 | 20.9 |

A double-cylinder type reactor (Figure 4-16) including an oxidizing section in the center and a scrubbing section in the outer part has been developed recently. The absorbing liquor goes down the scrubbing section, then goes up in the oxidizing section and overflows to the scrubbing section. The reactor allows some savings in floor space and investment cost.

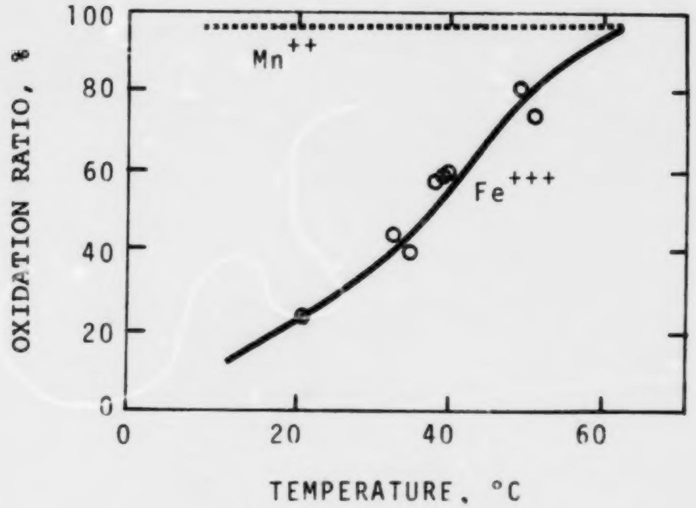


Figure 4-13. Temperature and oxidation ratio with catalysts.

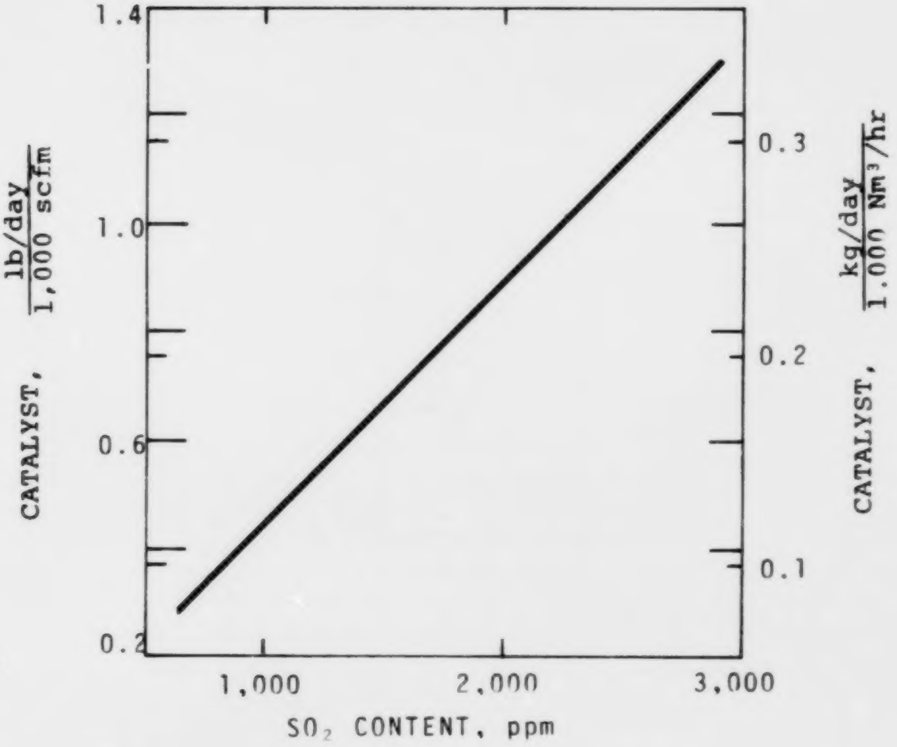


Figure 4-14. Catalyst consumption.

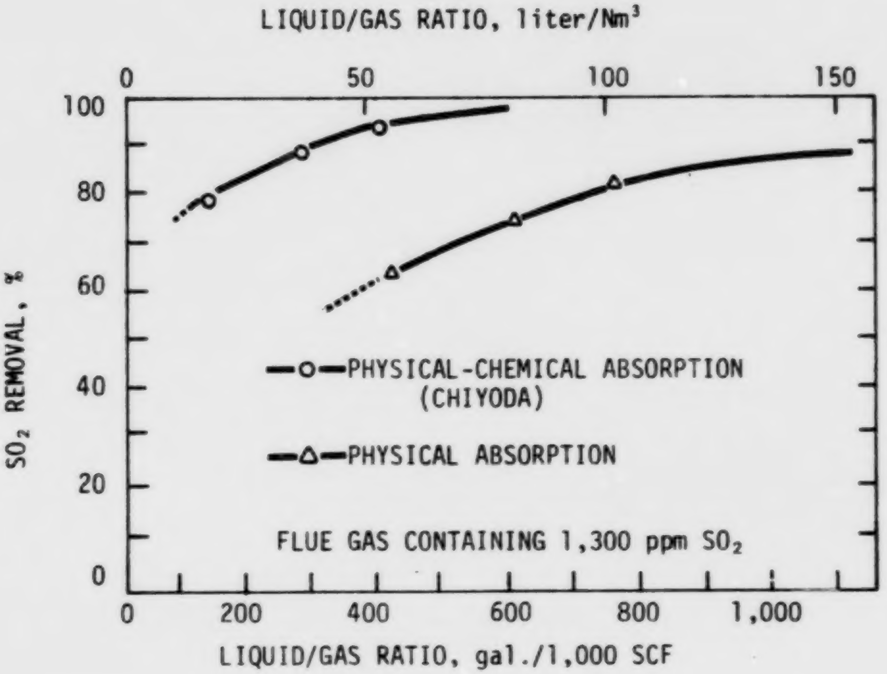


Figure 4-15. Liquid/gas ratio and $SO_2$ removal.

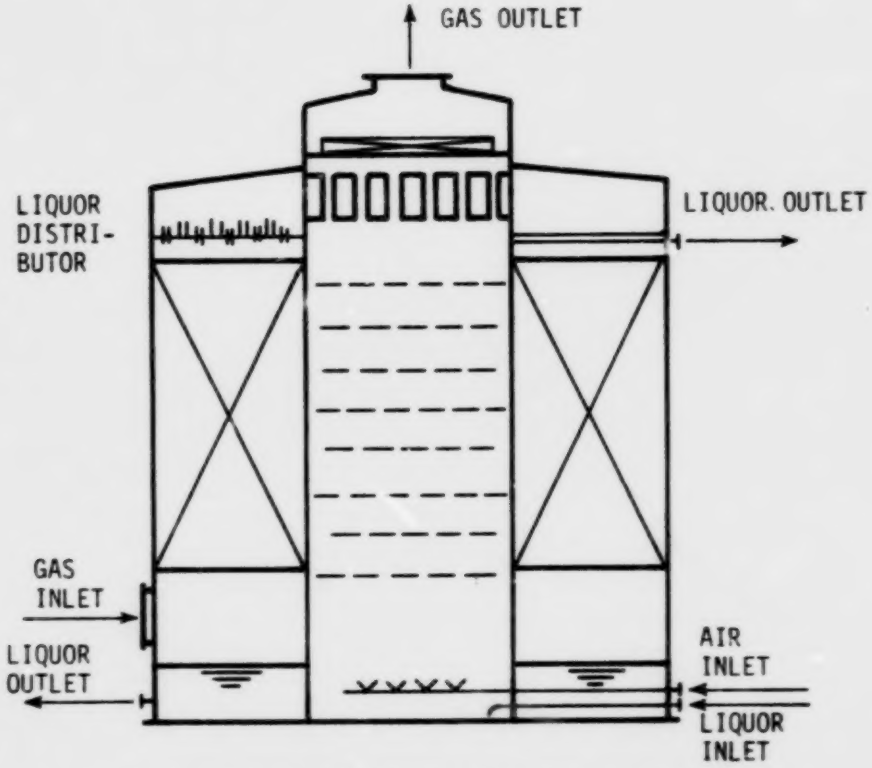

GAS OUTLET
LIQUOR DISTRIBUTOR
LIQUOR OUTLET
GAS INLET
LIQUOR OUTLET
AIR INLET
LIQUOR INLET

Figure 4-16. Double-cylinder type reactor.

## Performance

Except for minor early troubles, the Toyama plant, Hoduriku Electric, (750,000 $Nm^3$/hr) has been in smooth continuous operation since its start-up in May 1974 (Figures 4-17 and 4-18). $SO_2$ concentrations are about 600 ppm in the inlet gas, 40 ppm in the scrubber outlet, and 60 ppm after reheating to 145°C. The particulate contents are 20 to 30, 5 to 10, and 20 to 30 mg/$Nm^3$, respectively. An L/G ratio of 30 liters/$Nm^3$ (about 210 gal./1000 scf) is used. The power requirement is 4500 to 5000 kW at full-load operation treating 500 to 600 ppm $SO_2$. Wastewater (10 to 20 t/hr) is emitted to maintain the chloride concentration of the liquor under a certain level. Gypsum grows into large crystals (Figure 6-7, M); moisture content is 6 to 8 percent after the gypsum is centrifuged.

Other plants using the Chiyoda process have also operated well. For example, Aboshi plant, Daicel Co., has been in smooth operation since its start-up in November 1973. The plant uses the two-tower system (Figure 4.19) and treats flue gas from an oil-fired boiler at a rate of 100,000 $Nm^3$/hr. $SO_2$ is reduced from 1500 ppm to 80 to 100 ppm at an L/G ratio of about 40 (about 300 gal./1000 scf) and the gas velocity in the absorber is 0.6 m/sec. The air requirement for oxidation has been about 5 times stoichiometric; the air flow is about 2000 $m^3$/hr. Gypsum crystals are smaller than those by-produced at the Toyama plant (Figure 6-7, N) and the gypsum contains about 10 percent moisture after being centrifuged. The product is gray, containing a small amount of carbon dust. Still it is sold for wallboard production. It was intended to purge wastewater at a rate of 0.5 t/hr to keep the magnesium concentration under control. However, since the oil contains 30 to 40 ppm chloride and the make-up water contains 20 to 30 ppm, such a purge would allow the chlorine concentration in the circulation liquor to go as high as 1000 ppm, which is considered too high from the

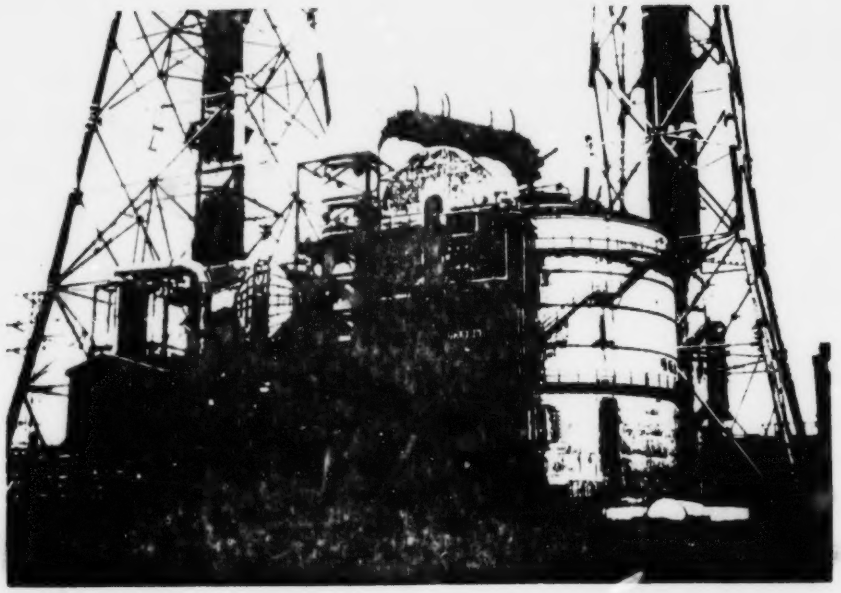


Figure 4-17. Toyama plant, Hokuriku Electric (Reactor and prescrubber).

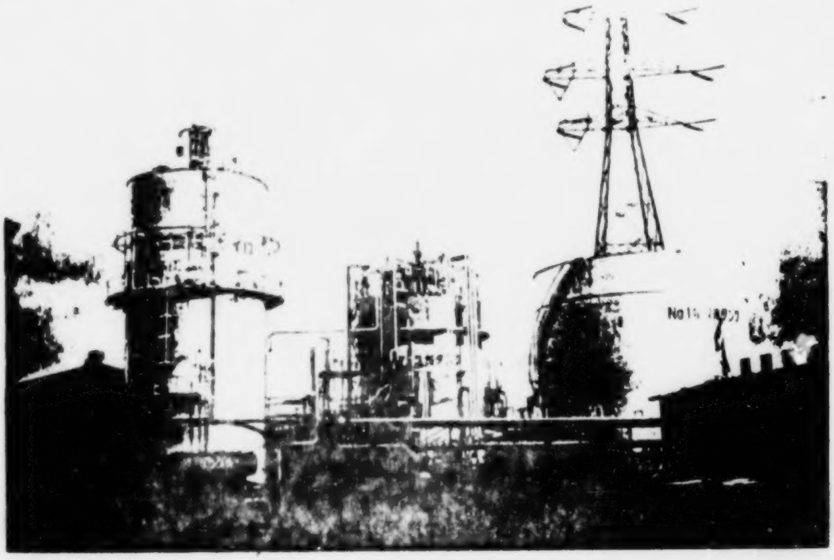

Limestone tank
Crystallizer
Sulfuric acid tank

Figure 4-18. Toyama plant, Hokuriku Electric.

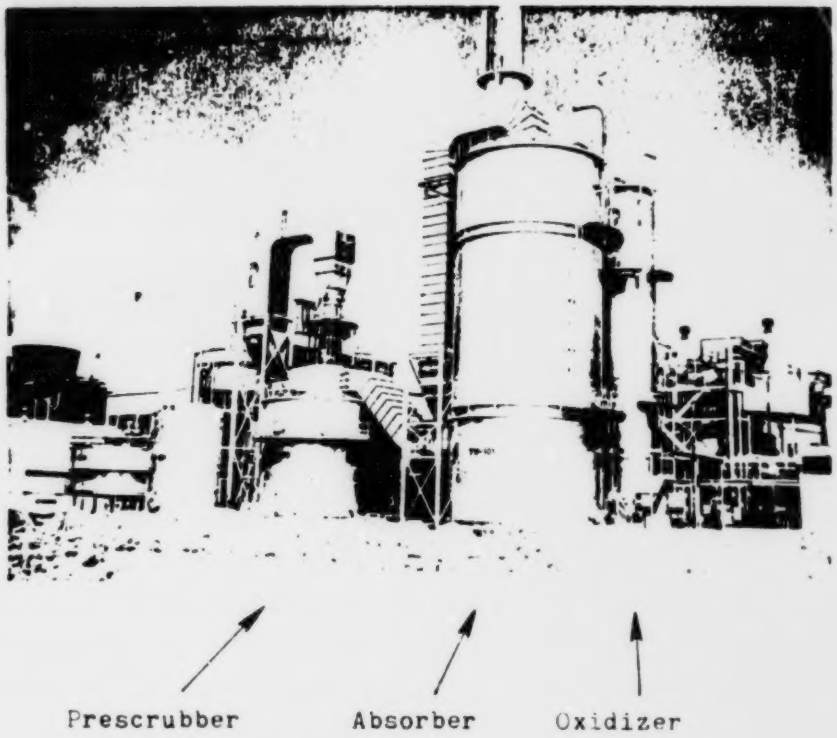

Prescrubber
Absorber
Oxidizer

Figure 4-19. Abosi plant, Daicel Co.

standpoint of stress corrosion. The current purge is 2 t/hr of liquor at pH 6 to 8. Total water make-up is 20 t/hr.

### Economics

The capital cost was about $30/kW at the time of construction between December 1971 and April 1973. With recent sharp inflation, the cost would be $65 to 70 at present. The Hokuriku plant is operated by two operators per shift. The requirements at 95 percent load operation are process water 64 t/hr, fuel for reheating 3 t/hr, steam 1.5 t/hr, and limestone 1.5 t/hr. The amount of by-product gypsum is 2.7 t/hr at full load. The desulfurization cost including depreciation (15 percent yearly) is $13/kl oil for the Toyama plant and $20/kl for the new plants to be constructed.

### Evaluation

The process is simple and the plant is easy to operate. Even in the event that the gypsum-producing system must be stopped for a day or two for repairs, the absorbing system can be operated continuously. The concentration of sulfuric acid increases by 1 or 2 percent in this case, but $SO_2$ recovery is not decreased. Catalyst is cheap and is not poisoned by impurities in the gas. Salable gypsum of good quality is obtained from limestone without scaling problems.

Disadvantages are that large pumps and a fairly large scrubber and oxidizer are required. Operation of the new plant of Gulf Power Co. in Florida will allow evaluation of applicability of this process to coal-fired boilers.

## DOWA ALUMINUM SULFATE PROCESS

### Outline of the Process

This aluminum sulfate process has been developed by Dowa Mining Co. Dowa is one of the largest manufacturer of nonferrous metals in Japan, owning many smelters and sulfuric acid plants. The aluminum sulfate process has been developed to desulfurize waste gas from smelters, roasters, and sulfuric acid plants. The principle of the process is as follows:

$SO_2$ is absorbed in a solution of basic aluminum sulfate, $Al_2(SO_4)_3 \cdot Al_2O_3$, of pH 3 to 4 to form $Al_2(SO_4)_3 \cdot Al_2(SO_3)_3$. The liquor is oxidized by air into $Al_2(SO_4)_3$, which is then treated with powdered limestone to precipitate gypsum and to regenerate the basic aluminum sulfate solution.

Absorption: $Al_2(SO_4)_3 \cdot Al_2O_3 + 3SO_2 = Al_2(SO_4)_3 \cdot Al_2(SO_3)_3$
Oxidation: $Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + 3/2\ O_2 = Al_2(SO_4)_3 \cdot Al_2(SO_3)_3$
Neutralization: $Al_2(SO_4)_3 \cdot Al_2(SO_4)_3 + 3CaCO_3 + 6H_2O =$
$Al_2(SO_4)_3 \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 3CO_2$

## State of Development

After tests with a pilot plant with a capacity of 300 $Nm^3$/hr, a small commercial plant (3300 $Nm^3$/hr) was constructed at the Mobara Works of Taenaka Mining and started operation in October 1972 to treat waste gas from a molybdenum sulfide roaster containing 7500 ppm $SO_2$ at 100°C. Two commercial units, each with a capacity of treating 150,000 $Nm^3$/hr of tail gas from a sulfuric acid plant, have been built at Okayama Works of Dowa. One started operation in June and the other in September 1974. A pilot plant with a capacity of treating 3000 $Nm^3$/hr of flue gas from an oil-fired boiler has also been in operation. Mitsui Shipbuilding Co. recently joined Dowa for further development of the process.

## Absorbing Liquor

The relations between the composition of basic aluminum sulfate liquor (Table 4-8) and $SO_2$ absorbing capacity and the boiling point of the liquor after the $SO_2$ absorption are shown in Figures 4.20 and 4.21.

Table 4-8. COMPOSITION OF SOLUTIONS IN FIGURES 4.20 AND 4.21

| No. | $Al_2O_3$ in solution g/l | | | Basicity, % |
|---|---|---|---|---|
| | Free | Combined | Total | |
| I | 34.4 | 66.1 | 100.5 | 34.2 |
| II | 40.0 | 58.2 | 98.2 | 40.8 |
| III | 45.5 | 53.2 | 98.7 | 46.1 |

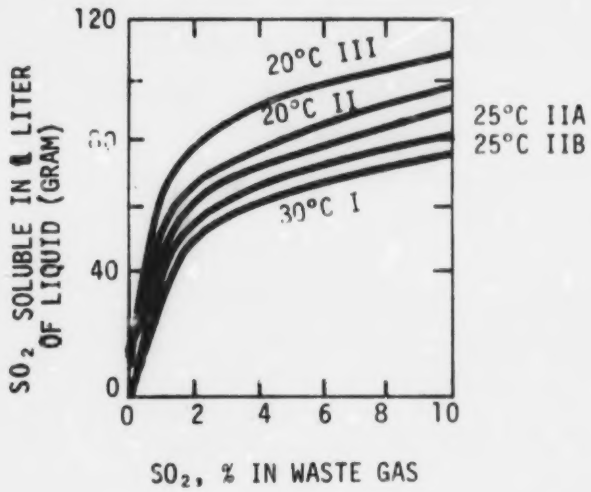


Figure 4-20. $SO_2$ absorbing capacity of the liquors.

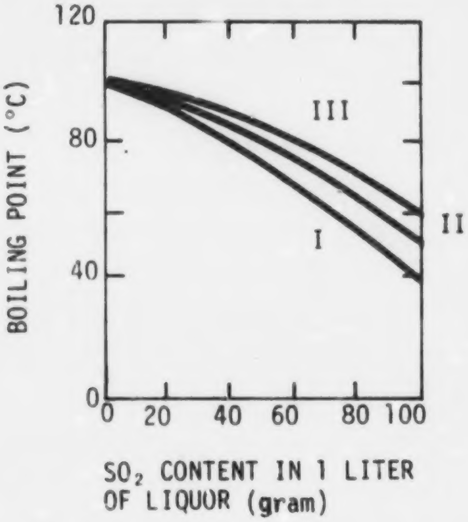


Figure 4-21. Boiling point of the liquor containing $SO_2$.

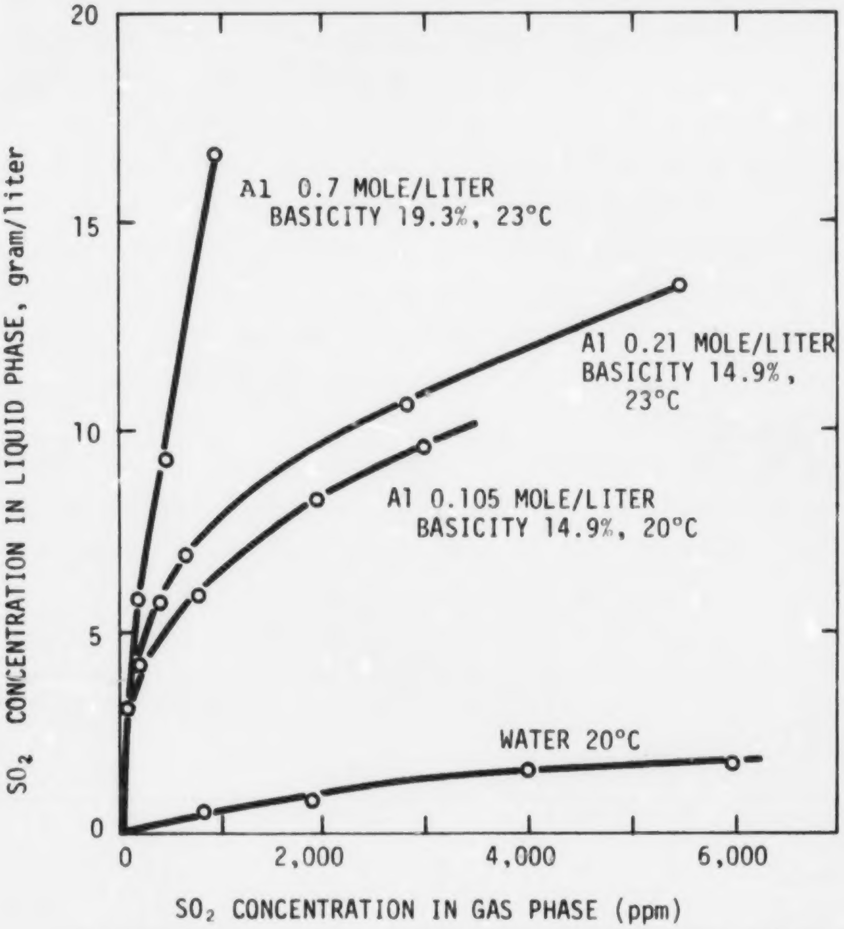


Figure 4-22. $SO_2$ absorbing capacity of dilute liquors.

Optimum concentration as well as basicity of the absorbing liquor are selected according to the $SO_2$ concentration of the gas and the removal efficiency required. Normally liquors at pH 3 to 4, which are more dilute than those shown in Table 4-8 are used. The relations between the composition and $SO_2$ absorbing capacity of the dilute liquors are shown in Figure 4-22.

Figures 4-20 and 4-22 show the $SO_2$ absorbing capacity of liquors at 20 to 30°C for the treatment of tail gas from a sulfuric acid plant. For treatment of flue gas the liquid temperature normally reaches 55 to 60°C and thus the $SO_2$ absorbing capacity is considerably lowered.

## Process Description

A flowsheet of the process is shown in Figure 4-23. The waste gas is led into an absorber--a TCA scrubber at the Taenaka plant and a packed tower at the Okayama plant. Each has a spray for cooling in the lower part. The liquor from the absorber is led into a tank to which make-up aluminum sulfate is added. The liquor from the tank is sent to an oxidizer, where aluminum sulfite is oxidized into sulfate by small bubbles of air. The oxidizer, which has no moving parts, has been developed by Dowa. Twice the stoichiometric amount of air is used (in design). Most of the oxidized solution is returned to the absorber; a portion is sent to a neutralizer and treated with powdered limestone (mostly under 200 mesh) under conditions suitable for the crystal growth of gypsum.

The slurry from the neutralizer passes through the thickener and is then centrifuged. All of the liquor from the thickener and the centrifuge as well as the wash water of the gypsum are returned to the absorber.

For treatment of flue gas, a cooler is installed to cool the gas temperature to 80°C using a portion of the scrubber liquor. A packed tower is used for the scrubbing.

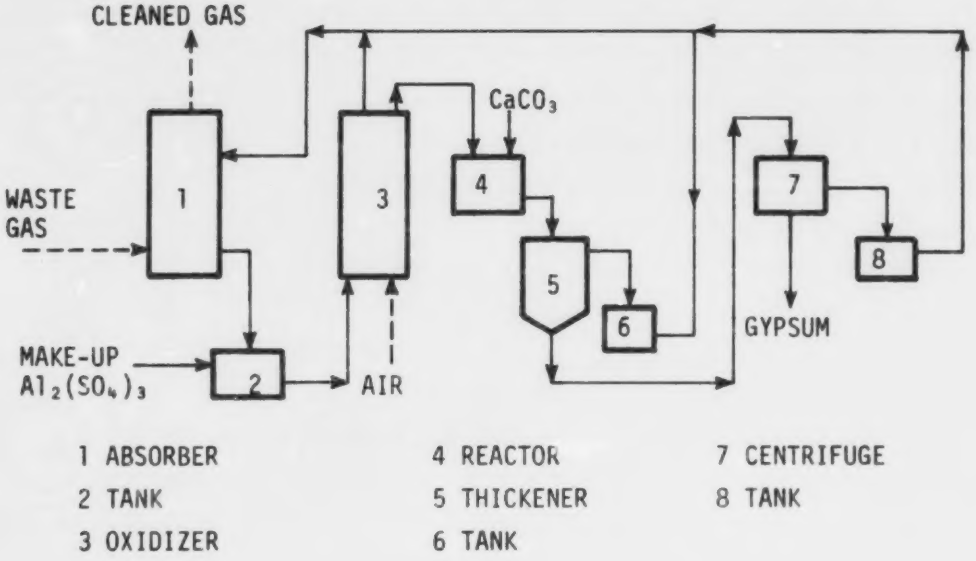

CLEANED GAS
WASTE GAS
MAKE-UP
$Al_2(SO_4)_3$
AIR
$CaCO_3$
GYPSUM
1
2
3
4
5
6
7
8
1 ABSORBER
2 TANK
3 OXIDIZER
4 REACTOR
5 THICKENER
6 TANK
7 CENTRIFUGE
8 TANK

Figure 4-23. Flowsheet of Dowa aluminum sulfate - limestone process.

## Performance

The Taenaka plant has been in operation since October 1972 recovering more than 95 percent of the $SO_2$ (7500 ppm) at an L/G ratio of 5 liters/$Nm^3$ (35 gal./1000 scf). There is no appreciable problem of scaling. The pipings required cleaning once every several months during the early operation to remove soft deposits, but no cleaning has been needed since 1974.

The units at Okayama (Figures 4-24 and 4-25) have been in smooth continuous operation since their start-up in June and September 1974, except for a scheduled stop of the first unit for one day in October for inspection, in which no problem was observed. $SO_2$ concentration at the inlet has ranged from 400 to 700 ppm and at the outlet from 2 to 29 ppm at an L/G ratio of 2.5 liters/$Nm^3$ and liquor temperature of 25°C. The gas velocity in the tower is 1.3 m/sec. A plastic-packed mist eliminator is placed at the top of the absorber. No reheating of the gas is required because the temperature is close to the outside temperature and no plume is formed. The $O_2$ concentration of the inlet gas is about 5 percent. About two-thirds of the absorbed $SO_2$ is oxidized in the absorber; the remarkable oxidation is caused by catalytic action of a small amount of ferric ion. Thus the amount of air to the oxidizer has been substantially reduced from the design value, which was twice that of the $SO_2$ absorbed. The concentration of magnesium in the liquor has also increased slightly during the operation but no wastewater has yet been purged.

Tests with a flue gas from the burning of heavy oil, the gas containing 1500 to 1700 ppm $SO_2$, have indicated that an L/G ratio of about 8 is required to recover 95 percent $SO_2$. Addition of a small amount of a soluble metallic catalyst has lowered the L/G ratio to 5 for 95 percent recovery. The catalyst promotes not only $SO_2$ absorption but also oxidation. Tests with a flue gas containing 7 to 8

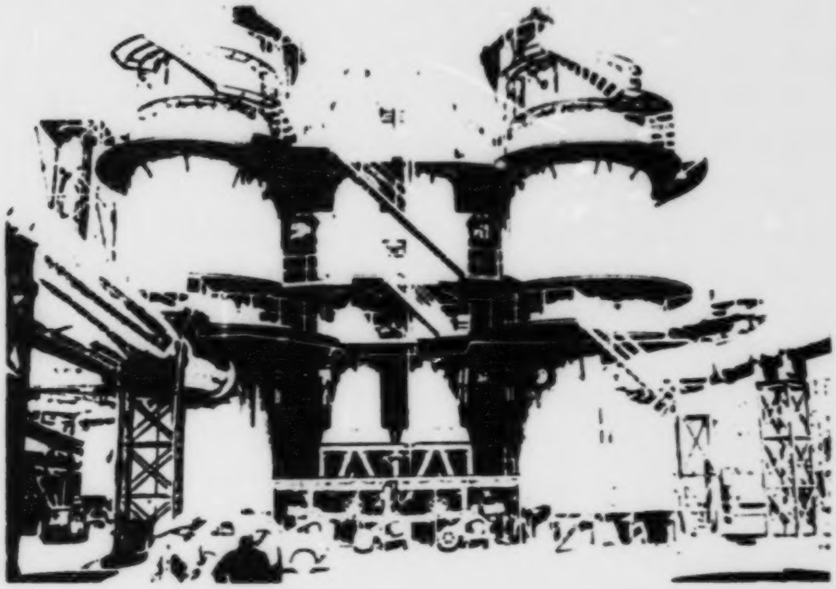


Figure 4-24. Okayama plant, Dowa Mining Absorbers (both sides), oxidizers (middle).

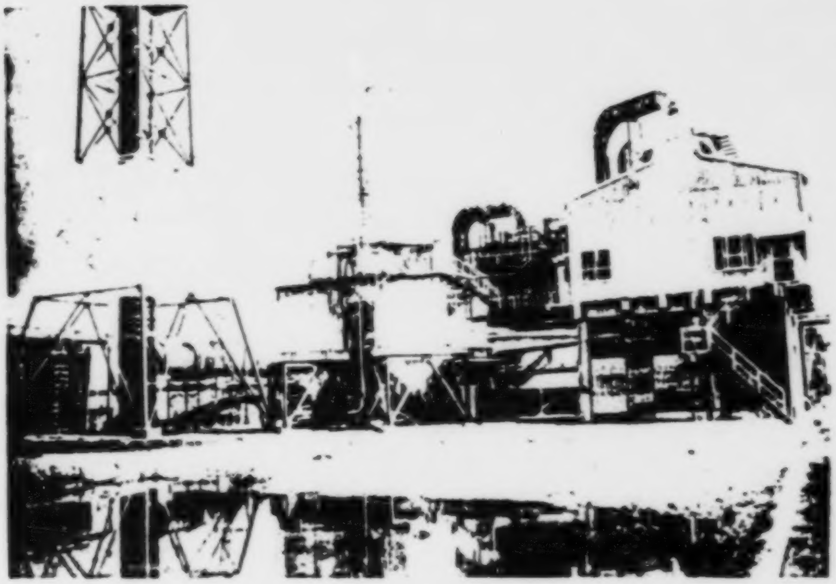


Figure 4-25. Okayama plant, Dowa Mining (Reactors and thickeners).

percent oxygen using the catalyst have indicated that oxidation occurred completely in the absorber and thus the oxidizing tower may not be needed.

If some wastewater must be purged to reduce impurities such as chloride and magnesium, a portion of the liquor will be neutralized with lime to precipitate hydroxides of aluminum and the metallic catalyst, which will be returned to the system.

A small amount of aluminum is contained in the gypsum but does not affect the quality of wallboard and cement produced from the gypsum. The aluminum concentration is about 0.5 kg per ton of gypsum.

Economics

Investment cost (in late 1974) is about \$18/Nm$^3$/hr or \$55/kW. Following are operating requirements for the plant, which treats 300,000 Nm$^3$/hr of tail gas containing 650 ppm $SO_2$:

| | | |
|---|---|---|
| $CaCO_3$ | 0.714 t/hr | \$15/t |
| $Al_2(SO_4)_3$ solution ($Al_2O_3$ 8%) | 15 kg/hr | 4¢/kg |
| Water | 7.1 t/hr | 3.3¢/t |
| Electricity, about 1000 kW (may be reduced to 600 kW) | | 3.7¢/kw |
| Operator | 1 per shift | |

These values indicate that both the investment and the operating costs are fairly low.

Evaluation

The process is simple and the plant is easy to operate. Limestone is used, and more than 95 percent of the $SO_2$ is removed at a relatively low L/G ratio. Essentially no scaling occurs and no wastewater is generated. Investment and running costs are low. These features indicate that this process is promising also for flue gas treatment.

## KURABO AMMONIUM SULFATE LIME PROCESS[6]

In this process developed by Kurabo Industries, Ltd. $SO_2$ is absorbed by a slightly acidic ammonium sulfate solution at pH 3 to 4. The solution is then oxidized by air to give an acidic ammonium sulfate solution, which is then treated with lime to precipitate gypsum and to allow recovery of aqua ammonia, which is returned to the absorbing system. Ammonium sulfate can be produced, if desired.

### State of Development

Kurabo has built several small ammonia scrubbing plants in addition to many sodium scrubbing plants. Plume formation, the greatest problem with ammonia process, has been fairly well solved by the use of a cold, dilute solution; this method may not be suitable for larger plants, however. Kurabo has recently developed a method to use an acidic ammonium sulfate solution as the absorbent to eliminate the plume and has successfully operated a 2-MW equivalent test unit. Four commercial plants are presently under construction (Table 4-9).

Table 4-9. PLANTS USING THE KURABO AMMONIUM SULFATE LIME PROCESS

| User | Plant site | Capacity, $Nm^3/hr$ | Date of completion |
|---|---|---|---|
| Kurarey | Tamashima | 100,000 | Jan. 1975 |
| Daicel | Aboshi | 163,000 | Mar. 1975 |
| Bridgestone | Tosu | 60,000 | Aug. 1975 |
| Bridgestone | Tochigi | 80,000 | Oct. 1975 |

### Theory of Absorption with Ammonium Sulfate Solution

Plume can be eliminated by use of an acidic absorbing liquor because the vapor pressure of $NH_3$ is less than 1 ppm with a solution at a pH lower than 4 (Figure 4-26). The acidic ammonium sulfate solution has a greater capacity for $SO_2$ absorption than plain water or a saturated calcium

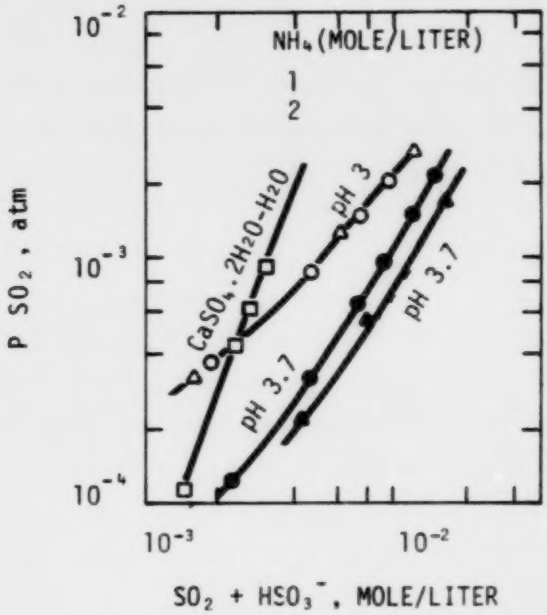


Figure 4-26. Relationship of $SO_2$ + $HSO_3$ concentration to partial pressure of $SO_2$ (60°C).

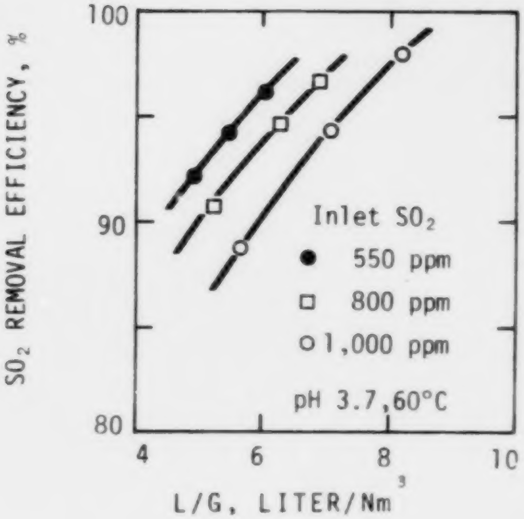


Figure 4-27. $SO_2$ removal efficiency at the test unit (5000 Nm$^3$/hr)

Tower diameter, 1 m
Packing height, 2 m
Packing Netring HA-18
Gas velocity 1.3-1.7 m/sec

sulfate solution, as shown in Figure 4-27, because of the smaller pH drop due to the following equilibrium in the ammonium sulfate solution:

$$H^+ + SO_4^{--} \rightleftarrows HSO_4^-$$

The minimum L/G ratio (liters/$Nm^3$) required to remove 95 percent of the $SO_2$ is shown in Table 4-10. Basic data for the design of $SO_2$ absorbers obtained through the pilot tests are shown in Table 4-11.

Table 4-10. MINIMUM L/G RATIO REQUIRED FOR 95 PERCENT $SO_2$ REMOVAL[a] (liter/$Nm^3$)

| Absorbing liquor | | Inlet $SO_2$ concentration, ppm | | |
|---|---|---|---|---|
| Composition | Initial pH | 1000 | 2000 | 3000 |
| $CaSO_4 \cdot 2H_2O$ - $H_2O$ | 7.0 | 14.0 | 21.2 | 27.2 |
| 0.25 mole/l $(NH_4)_2SO_4$ | 3.5 | 6.2 | 7.3 | 9.4 |
| 0.5 mole/l $(NH_4)_2SO_4$ | 3.5 | 5.1 | 5.8 | 7.2 |
| 1.0 mole/l $(NH_4)_2SO_4$ | 3.5 | 4.2 | 5.4 | 6.3 |

[a] At 60°C.

Table 4-11. DESIGN BASE OF $SO_2$ ABSORBER

| Packing | L/G ratio, liter/$Nm^3$ | Pressure drop, mm $H_2O$ | Space velocity, m/sec | Height of packing, m |
|---|---|---|---|---|
| Tellerette L type | 8 | 100 | 2 | 4 |
| Netring HA-18 | 8 | 100 | 1.5 | 3 |

Process Description

The flowsheet of the process is shown in Figure 4-28. Flue gas is first led into a KBCA scrubber and then into a packed tower absorber. The main function of the KBCA scrubber is to cool the gas to 60°C and to concentrate the absorbing

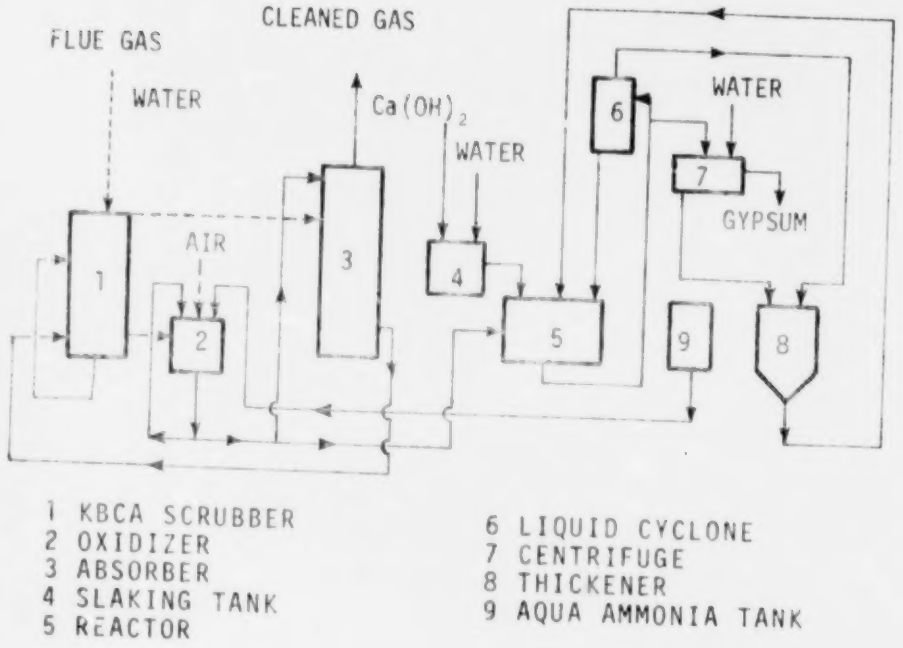

FLUE GAS
WATER
CLEANED GAS
Ca(OH)$_2$
WATER
AIR
WATER
GYPSUM
1
2
3
4
5
6
7
8
9
1 KBCA SCRUBBER
2 OXIDIZER
3 ABSORBER
4 SLAKING TANK
5 REACTOR
6 LIQUID CYCLONE
7 CENTRIFUGE
8 THICKENER
9 AQUA AMMONIA TANK

Figure 4-28. Flowsheet of Kurabo ammonium sulfate gypsum process.

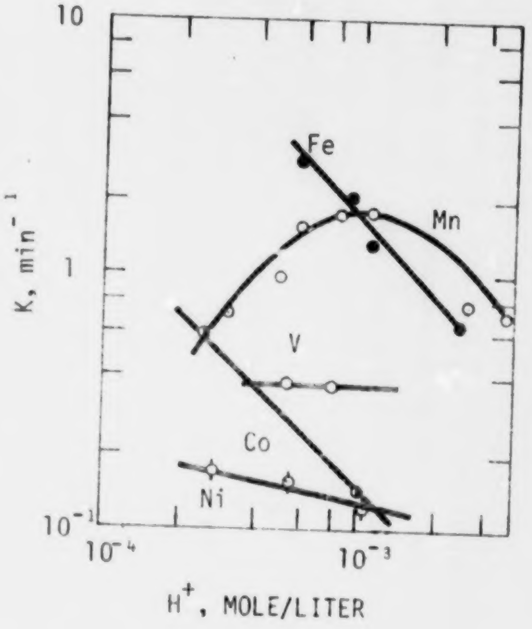


Figure 4-29. Oxidation rate of sulfite ion (40°C)

($HSO_3^+$)<10-2 mole/liter

( $M^{++}$) 2x10-4 mole/liter

liquor (ammonium sulfate solution). More than 90 percent of the $SO_2$ is removed. The gas is then reheated by the afterburning of oil. The liquor from the packed tower absorber is sent to the KBCA unit, concentrated, and then led into an oxidizer. The pH of the liquor in the oxidizer is adjusted to from 3 to 4 by adding dilute aqua ammonia and the sulfite in the liquor is oxidized into sulfate by small bubbles of air formed by introducing a jet stream of circulating liquor accompanying air into a pool of the liquor. About 5 times the stoichiometric amount of air is used. Tests have shown that $Fe^{++}$ catalyst gives an optimum oxidation rate at pH 4 and $Mn^{++}$ at pH 3 (Figure 4-29). Actually no catalyst is added for oxidation because it occurs fairly rapidly at a rate of 0.8 to 1.0 kg mole/$m^3$/hr; presumably small amounts of vanadium and iron derived from the fuel help the oxidation.

Arrangement of the Tamashima plant is shown in Figure 4-30. Most of the liquor from the oxidizer is returned to the absorber, and a portion is sent to a set of three reactors, where the liquor is treated with milk of lime to precipitate gypsum. In order to raise the concentration of the slurry and to increase the retention time of gypsum for better crystal growth, a portion of the slurry is sent to a liquid cyclone. The gypsum is returned to the reactor and the liquor, which contains some gypsum, is sent to a thickener. The overflow from the thickener is returned to the reactor, and the other portion of the slurry is sent to a centrifuge. The liquor from the centrifuge and wash water are sent to an aqua ammonia tank, and the aqua ammonia is sent to the oxidizer.

The concentration of the absorbing liquor is normally about 0.5 mole of ammonium sulfate per liter at an L/G ratio of 8 liter/$Nm^3$. It can be raised to 2.5 moles at the same L/G ratio without an appreciable decrease of $SO_2$ removal effi-

Reproduced from best available copy.

Figure 4-30. Tamashima plant, Kurarey (Kurabo process).

ciency. The amount of water added to the system, to dissolve lime and to wash gypsum, is usually less than that volatilized in the cooler. Therefore, some water is introduced into the cooler to maintain the water balance. Occasional purging may be required to prevent buildup of chloride. The by-product gypsum contains about 9 percent moisture with a bulk density of about 1.06 and pH 8. The average crystal size is 40 to 60 microns. The gypsum can be used as an additive for both wallboard and cement.

Ammonium sulfate can be obtained easily by concentrating the solution from the oxidizer. In this case, a nearly saturated solution (2.5 to 3 moles/liter) is used as the absorbent.

### Cost Estimation

A cost estimation is shown in Table 4-12.

### Evaluation

No plume is emitted, and no scaling occurs. Both oxidation and crystallization of gypsum are accomplished at 50 to 60°C without external heating. The pH of the liquor is kept over 3 to prevent corrosion. All steps are carried out at atmospheric pressure. A closed system can be achieved. Ammonium sulfate can be produced easily, if desired. The softening step of the circulating liquor is not needed.

Disadvantages are that the process is not simple, limestone cannot be used, and the L/G ratio is higher than for conventional ammonia scrubbing.

## OTHER INDIRECT LIME/LIMESTONE PROCESSES

### Tsukishima Sodium-lime Process

Tsukishima Kikai Co. (TSK) has constructed a plant using a sodium-lime double-alkali process (Figure 4-31) for Kinuura Utilities. The Nagoya plant (60 MW) started operation in June 1974 (Table 4-1). Sodium bisulfite formed by

### Table 4-12. ESTIMATED COSTS OF KURABO PROCESS[a]
(1 dollar = 300 yen)

| | By-product | |
|---|---|---|
| | Gypsum | Ammonium Sulfate |
| Investment cost, \$ thousands | 3,000 | 2,670 |
| Fixed cost, \$ thous./yr | | |
| Depreciation | 386 | 343 |
| Interest | 120 | 133 |
| Total | 506 | 476 |
| Running cost, \$ thous./yr | | |
| Ammonia, \$230/t | 6 | 443 |
| Lime, \$30/t | 95 | |
| Oil for reheating, \$100/kl | 153 | 153 |
| Industrial water, 3¢/$m^3$ | 2 | 3 |
| Power, 3¢/kWh | 143 | 143 |
| Steam, \$6.7/t | | 30 |
| Gypsum, \$6.7/t | -63 | |
| Ammonium sulfate, \$83/t | | -613 |
| Labor | 26 | 30 |
| Maintenance | 60 | 60 |
| Total | 422 | 249 |
| Total annual cost, \$ thousands | 928 | 725 |
| Desulfurization cost, \$/kl | 15.5 | 12.8 |

[a] Values at 1974 rates for a plant with capacity of 100,000 $Nm^3$/hr, burning 60,000 kl oil per year with 2.8 percent sulfur; operation at 8500 hours/year.

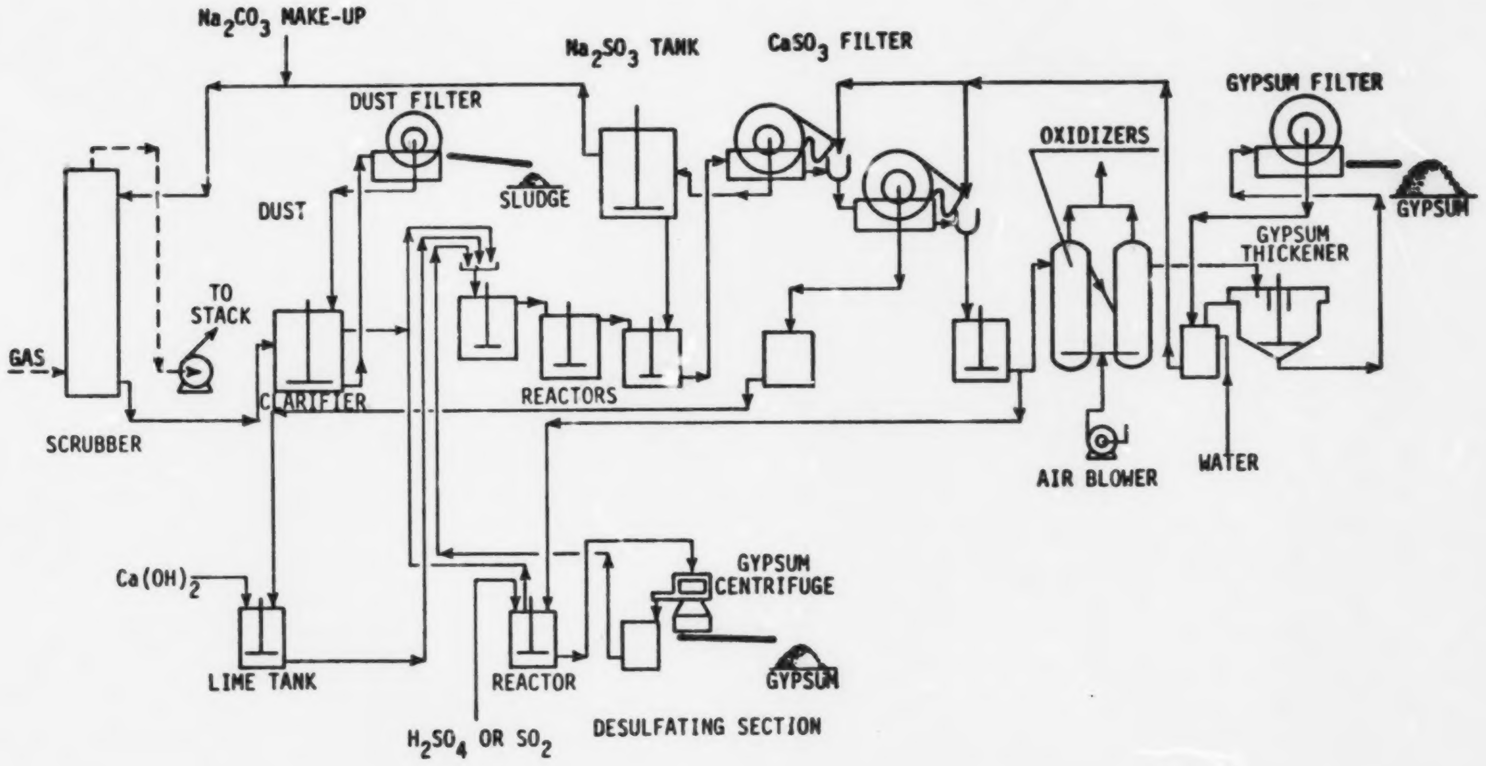

$Na_2CO_3$ MAKE-UP
DUST FILTER
$Na_2SO_3$ TANK
$CaSO_3$ FILTER
GYPSUM FILTER
OXIDIZERS
DUST
SLUDGE
GYPSUM
GYPSUM THICKENER
TO STACK
GAS
CLARIFIER
REACTORS
SCRUBBER
AIR BLOWER
WATER
$Ca(OH)_2$
GYPSUM CENTRIFUGE
LIME TANK
REACTOR
GYPSUM
$H_2SO_4$ OR $SO_2$
DESULFATING SECTION

Figure 4-31. Flowsheet of Tsukishima double-alkali process.

reaction of sodium sulfite and $SO_2$ is reacted with lime in three reactors in series to precipitate calcium sulfite and to regenerate sodium sulfite. Calcium sulfite is filtered, repulped, and oxidized by air into gypsum. Sodium sulfate formed by oxidation of the sodium sulfite is decomposed by reaction with the calcium sulfite and sulfuric acid, as in the Showa Denko process. $SO_2$ concentrations range from 750 to 1300 ppm at the inlet and from 90 to 120 ppm at the outlet.

A plant for Daishowa Paper Manufacturing Co. (Fuji plant, 85 MW) will be completed in June 1975. $SO_2$ concentrations will be 1300 ppm at the inlet and 60 ppm at the outlet. Sodium sulfate will be separated from the liquor by cooling and crystallization. About 0.5 t/hr of the sulfate will be obtained as a by-product.

### Hitachi-Tokyo Electric Carbon-Limestone Process

Hitachi Ltd. with Tokyo Electric Power has developed a dry carbon process.[3] A flue-gas desulfurization plant (150 MW) at the Kashima Station, Tokyo Electric Power, has been in operation using the process since 1972.[3] Dilute sulfuric acid (17 percent) is obtained by washing the carbon which has absorbed $SO_2$ with weak sulfuric acid and water and is treated with limestone to precipitate gypsum of good quality. The centrifuged supernatant liquor contains fine particles of gypsum, so fine that recycling for carbon washing would plug the carbon. Therefore, the liquor is sent to a wastewater treatment system and then purged.

As an alternative, the station has operated a 15-MW test unit in which the acid is concentrated to 50 to 70 percent by contact with the hot gases between the electrostatic precipitator and absorbers, and then reacted with powdered limestone. By the heat of reaction most of the water is eliminated to produce nearly dry gypsum, which is pelletized by extrusion to form cylindrical pellets about 20 mm in diameter and 50 mm long. The pellets are suitable for charging into a cement mill and also may be suitable for landfill or throwaway material.

A 3000 $Nm^3$/hr pilot plant using a carbon slurry as the absorbent has been operated successfully at Hitachi's main laboratory. The resulting $H_2SO_4$ is neutralized with limestone to give gypsum.

## Nippon Steel Chemical Sodium-Lime Process

Nippon Steel Chemical Co. constructed a sodium-lime double-alkali process plant with a capacity of treating 20,000 $Nm^3$/hr of flue gas from an oil-fired furnace in 1972.[3] The plant has been in operation by-producing a sludge consisting mainly of calcium sulfite, which is used for landfilling with other materials. There is no plan to build other plants.

# 5. OTHER PROCESSES FOR $SO_2$ RECOVERY

## INTRODUCTION

About one hundred relatively small sodium scrubbing plants are operating in Japan by-producing mainly sodium sulfite and some sodium sulfate. Those processes were reviewed in the 1973 technology status report[3], and not much progress has occurred since then. Major plants using other processes are listed in Table 5-1.

### Wellman-Lord Process

Many plants using the Wellman-Lord process have been constructed by Mitsubishi Chemical Machinery Co. (MKK) and also by Sumitomo Chemical Engineering Co. (SCEC). The reliability of the process has been well demonstrated. A main problem in the process is the oxidation of sodium sulfite into sulfate, which does not absorb $SO_2$. The sulfate must be removed from the system, resulting in the loss of sodium and the need for wastewater treatment.

### Magnesia Scrubbing

Three plants are operated, with different magnesium scrubbing processes, by Mitsui Mining, Onahama-Tsukishima, and Chemico-Mitsui. A common feature of these processes is the production of large $MgSO_3 \cdot 6H_2O$ crystals (200 microns or so), which are much easier to filter and dry than are the small $MgSO_3 \cdot 3H_2O$ crystals. Neither the Mitsui Mining nor Onahama plant has encountered any problem in the filtration and drying steps, which were troublesome at Boston Edison Co. The Idemitsu Kosan plant, which recently started operation of a process based on the Chemico-Mitsui process, returns the recovered $SO_2$ to a Claus furnace for sulfur production; the other plants by-produce sulfuric acid.

## Table 5-1. SULFUR DIOXIDE SCRUBBING INSTALLATIONS IN JAPAN THAT BY-PRODUCE SULFURIC ACID AND SULFUR

| Process developer | Absorbent | User | Plant site | MW[a] | Type of plant | Year of completion | By-product, tons/day |
|---|---|---|---|---|---|---|---|
| Wellman-MKK | $Na_2SO_3$ | Japan Synth. Rubber | Chiba | 70 | Industrial boiler | 1971 | $H_2SO_4$ 40 |
| Wellman-MKK | $Na_2SO_3$ | Chubu Electric | Nishinagoya | 220 | Utility boiler | 1973 | $H_2SO_4$ 80 |
| Wellman-MKK | $Na_2SO_3$ | Japan Synth. Rubber | Yokkaichi | 150 | Industrial boiler | 1974 | $H_2SO_4$ 40 |
| Wellman-MKK | $Na_2SO_3$ | Toyo Rayon | Nagoya | 103 | Industrial boiler | 1975 | $H_2SO_4$ 45 |
| Wellman-MKK | $Na_2SO_3$ | Mitsubishi Chem. | Mizushima | 186 | Industrial boiler | 1975 | $H_2SO_4$ 80 |
| Wellman-MKK | $Na_2SO_3$ | National Railways | Kawasaki | 217 | Industrial boiler | 1975 | $H_2SO_4$ 100 |
| Wellman-MKK | $Na_2SO_3$ | Kurashiki Rayon | Okayama | 127 | Industrial boiler | 1975 | $H_2SO_4$ 60 |
| Wellman-MKK | $Na_2SO_3$ | Company SKD | Yokkaichi | 124 | Industrial boiler | 1977 | $H_2SO_4$ 55 |
| Wellman-SCEC | $Na_2SO_3$ | Toa Nenryo | Kawasaki | 23 | Claus furnace | 1971 | S |
| Wellman-SCEC | $Na_2SO_3$ | Sumitomo Chiba Chem. | Chiba | 120 | Industrial boiler | 1973 | $H_2SO_4$ 50 |
| Wellman-SCEC | $Na_2SO_3$ | Fuji film | Fuji | 50 | Industrial boiler | 1974 | Liquid $SO_2$ 12 |
| Wellman-SCEC | $Na_2SO_3$ | Sumitomo Chiba Chem. | Chiba | 180 | Industrial boiler | 1975 | $H_2SO_4$ 80 |
| Wellman-SCEC | $Na_2SO_3$ | Sumitomo Chem. | Niihama | 50 | Industrial boiler | 1975 | $H_2SO_4$ 23 |
| Ohahama-Tsukishima | MgO | Onahama Smelter | Onahama | 28 | Copper smelter | 1972 | $H_2SO_4$ 220 |
| Mitsui Mining | MgO | Mitsui Mining | Hibi | 25 | $H_2SO_4$ plant | 1971 | $H_2SO_4$ 16 |
| Chemico-Mitsui | MgO | Idemitsu Kosan | Chiba | 162 | Claus and boiler | 1974 | S |
| Sumitomo Shipbuilding | Carbon | Kansai Electric | Sakai | 53 | Utility boiler | 1971 | $H_2SO_4$ 15 |
| Shell | CuO | Showa Yokkaichi | Yokkaichi | 45 | Industrial boiler | 1974 | S |
| Mitsubishi-IFP | $(NH_4)_2SO_3$ | Maruzen Oil | Shimozu | 14 | Claus furnace | 1974 | S |
| TEC-IFP | $(NH_4)_2SO_3$ | Fuji Oil | Chiba | 3 | Claus furnace | 1974 | S |

[a] Actual for boilers and equivalent gas flow for others. Boilers are oil-fired.

### Ammonia Scrubbing-IFP Processes

Two relatively small plants, each with an ammonia scrubber and IFP reactor to by-produce elemental sulfur, were constructed by Mitsubishi Heavy Industries and Toyo Engineering. Both have encountered problems and are now being improved.

### Dry Processes

Three dry processes are being applied to prototype plants: two activated-carbon processes by Hitachi-Tokyo Electric and by Sumitomo Shipbuilding, and the Shell copper oxide process. In addition, pilot plants using the dry sodium absorption process followed by the decomposition of the resulting sodium sulfate have been operated by Tsukishima Kikai Co. and by the National Research Institute of Pollution and Resources. Mitsubishi Heavy Industries and Chubu Electric Power have recently given up the activated-manganese process because of the difficulty in achieving 90 percent recovery and the economical disadvantage.

## WELLMAN-MKK SODIUM PROCESS

### State of Development

Mitsubishi Chemical Machinery Co. (MKK) has constructed several desulfurization plants using the Wellman-Lord process (Table 5-1).

### Process Description[9]

A flowsheet and layout of the plant at Nishinagoya Station, Chubu Electric Power, are shown in Figures 5-1 and 5-2. The plant has a capacity of treating 620,000 $Nm^3/hr$ of flue gas from a 220-MW boiler which burns 3 percent sulfur oil. Specifications for the main equipment are shown in Table 5-2. The flue gas passing through an electrostatic precipitator is water-washed and cooled to 58°C in a pre-cooling section in the lower part of a scrubber and then passed through an absorbing section (three stages of sieve trays) to wash with a sodium sulfite solution

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3.$$

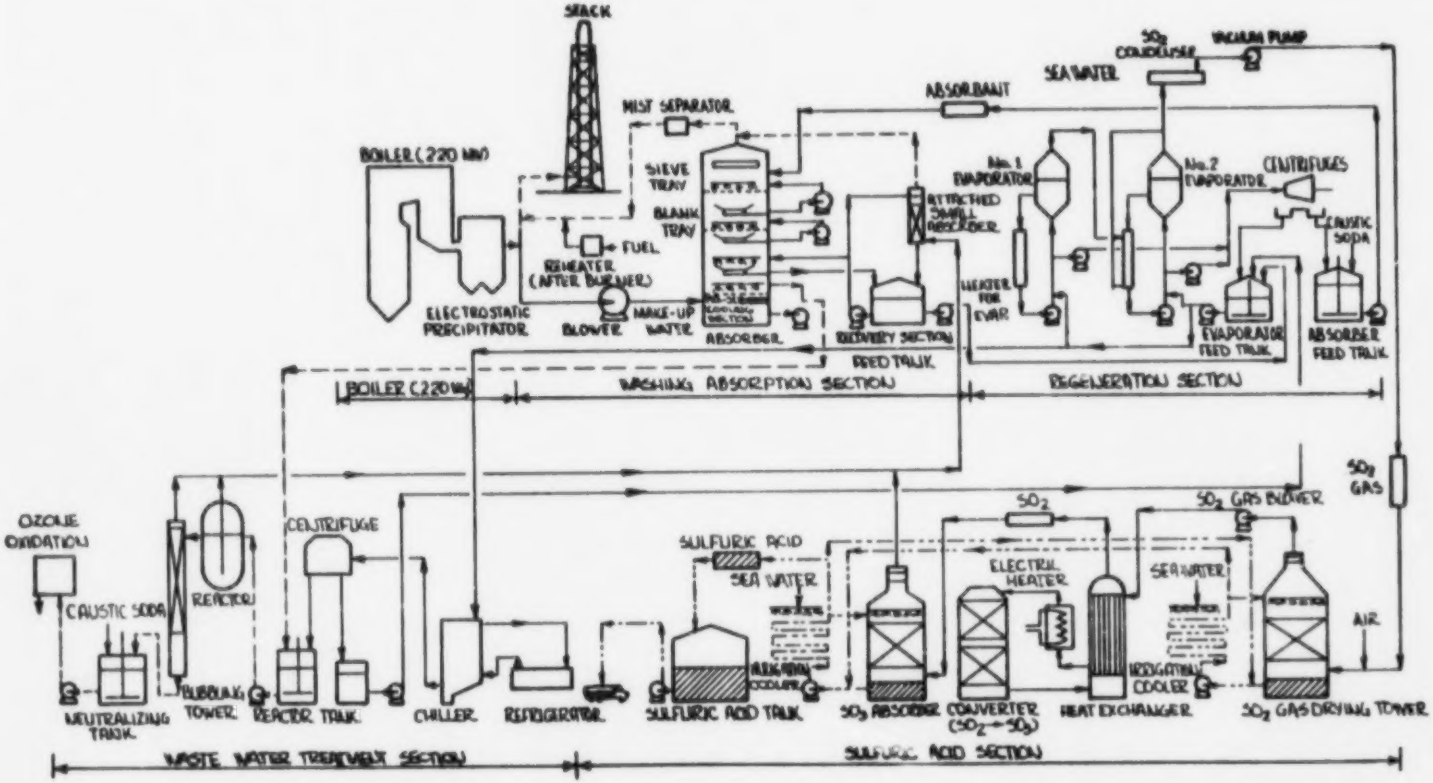

STACK
MIST SEPARATOR
BOILER (220 MW)
SIEVE TRAY
BLANK TRAY
FUEL
REHEATER (AFTER BURNER)
ELECTROSTATIC PRECIPITATOR
BLOWER
MAKE-UP WATER
COOLING SECTION
ABSORBER
ABSORBANT
SEA WATER
$SO_2$ CONDENSER
VACUUM PUMP
ATTACHED SMALL ABSORBER
RECOVERY SECTION FEED TANK
HEATER FOR EVAP.
No. 1 EVAPORATOR
No. 2 EVAPORATOR
CENTRIFUGES
CAUSTIC SODA
EVAPORATOR FEED TANK
ABSORBER FEED TANK
BOILER (220 MW)
WASHING ABSORPTION SECTION
REGENERATION SECTION
$SO_2$ GAS
OZONE OXIDATION
CAUSTIC SODA
REACTOR
CENTRIFUGE
NEUTRALIZING TANK
BUBBLING TOWER
REACTOR TANK
CHILLER
REFRIGERATOR
SULFURIC ACID
SEA WATER
SULFURIC ACID TANK
IRRIGATION COOLER
$SO_3$ ABSORBER
$SO_2$
ELECTRIC HEATER
CONVERTER ($SO_2 \rightarrow SO_3$)
HEAT EXCHANGER
SEA WATER
IRRIGATION COOLER
$SO_2$ GAS BLOWER
AIR
$SO_2$ GAS DRYING TOWER
WASTE WATER TREATMENT SECTION
SULFURIC ACID SECTION

Figure 5-1. Flowsheet of the Wellman-MKK process (Nishinagoya Station, Chubu Electric Power).

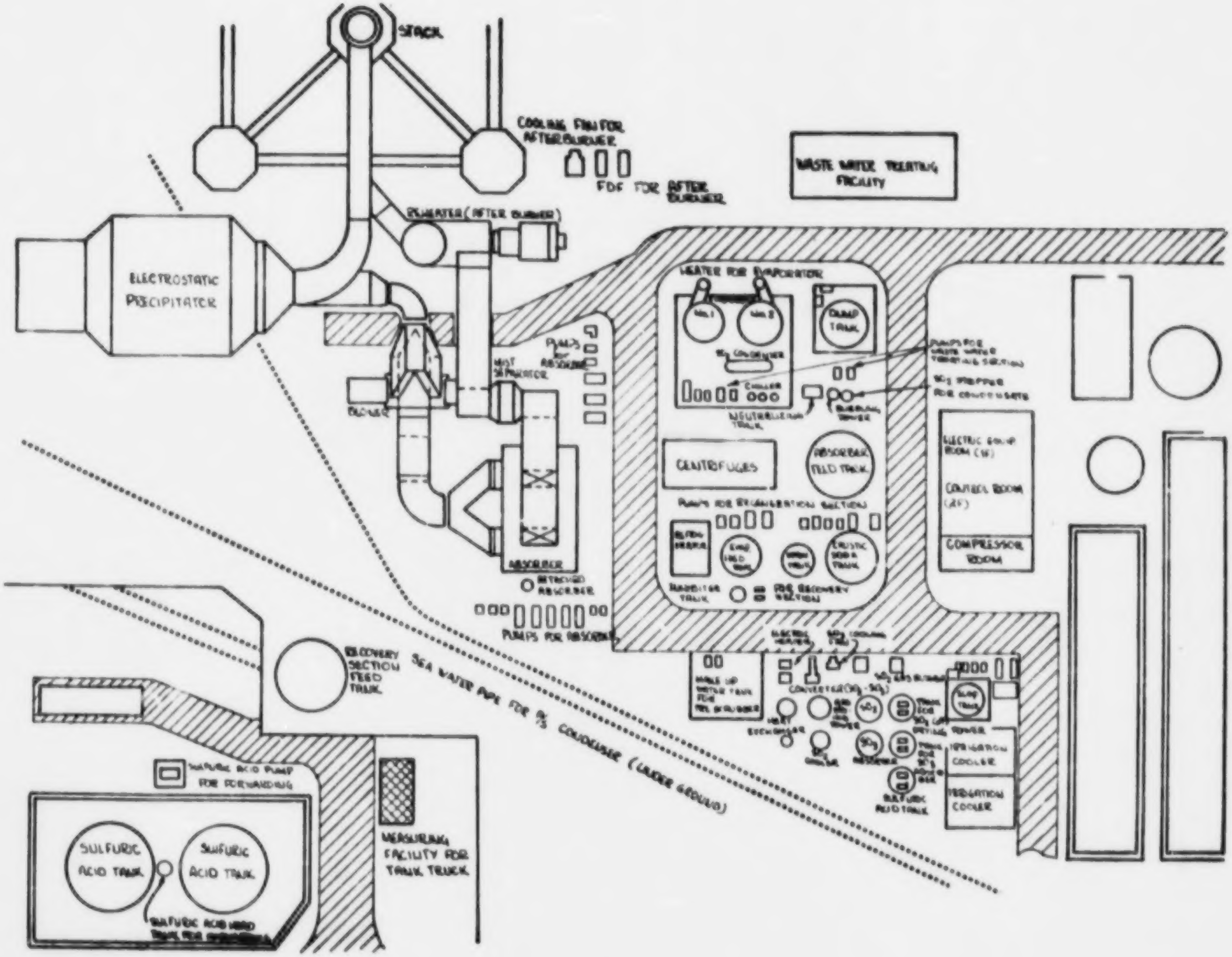

STACK
COOLING FAN FOR AFTERBURNER
FDF FOR AFTER BURNER
WASTE WATER TREATING FACILITY
REHEATER (AFTER BURNER)
ELECTROSTATIC PRECIPITATOR
BLOWER
MIST SEPARATOR
PUMPS FOR ABSORBER
ABSORBER
RETAINED ABSORBER
PUMPS FOR ABSORBER
HEATER FOR EVAPORATOR
No. 1
No. 2
$SO_2$ CONDENSER
CHILLER
NEUTRALIZATION TANK
DUMP TANK
PUMPS FOR WASTE WATER TREATING SECTION
$SO_2$ STRIPPER FOR CONDENSATE
BUBBLING TOWER
CENTRIFUGES
ABSORBER FEED TANK
PUMPS FOR REGENERATION SECTION
CAUSTIC SODA TANK
FOR RECOVERY SECTION
ELECTRIC GROUP ROOM (1F)
CONTROL ROOM (2F)
COMPRESSOR ROOM
ELECTRIC HEATER
$SO_2$ COOLING TANK
MAKE UP WATER TANK FOR
CONVERTER ($SO_2$ - $SO_3$)
HEAT EXCHANGER
$SO_3$
TOWER
IRRIGATION COOLER
IRRIGATION COOLER
SULFURIC ACID TANK
RECOVERY SECTION FEED TANK
SEA WATER PIPE FOR $SO_3$ CONDENSER (UNDER GROUND)
SULFURIC ACID PUMP FOR FORWARDING
SULFURIC ACID TANK
SULFURIC ACID TANK
MEASURING FACILITY FOR TANK TRUCK

Figure 5-2. Layout of the FGD plant at Nishinagoya Station.

Table 5-2. SPECIFICATIONS FOR MAIN EQUIPMENT

(NISHINAGOYA PLANT, CHUBU ELECTRIC)

| Name of equipment | Item | Specification |
|---|---|---|
| Absorber | Type | Rectangle, sieve-tray system |
| | Capacity | 620,000 $Nm^3/hr$ x 1 unit |
| | Size | 9m x 14m x 25.7m (height) |
| Fan and duct | Type | Centrifugal blade-type fan |
| | Capacity | 660,000 $Nm^3/hr$ x 1 unit |
| | Wind press | 650 mm $H_2O$ |
| Evaporator | Type | Vertical cylinder type |
| | Capacity | 18.3 t/hr x 1  16.4 t/hr x 1 |
| | Main size | 4.4 mØ x 917m (height) |
| Evaporator-heater | Type | Vertical, single current type by placed |
| | Main size | 1.7mØ x 10m (height) x 2 units |
| Evaporator-circulation pump | Type | Axial-flow pump |
| | Capacity | 9700 $m^3/hr$ |
| | Total head | 2.5m |
| Absorption liquid supply tank | Type | Vertically-placed cylindrical type |
| | Capacity | 412 $m^3$ x 1 unit |
| | Main size | 8.5mØ x 9.7 m (height) |
| Regenerative liquid tank | Type | Cone-roof |
| | Capacity | 487 $m^3$ x 1 unit |
| | Main size | 9.3mØ x 8.2m (height) |
| Convertor | Type | Vertically-placed cylindrical type |
| | Press. Temp. | 0.2 $kg/cm^2$  435 - 632°C |
| | Main size | 2.6mØ x 8.9m (height) |
| Sulfuric acid tank | Type | Cone-roof |
| | Capacity | 925 $m^3$ x 2 units |
| | Main size | 9.7 mØ x 10.7m (height) |

The pH and composition of absorbing liquor are as follows:

| | pH | $Na_2SO_3$, % | $NaHSO_3$, % | $Na_2SO_4$, % |
|---|---|---|---|---|
| Inlet | 7.3 - 7.5 | 20 | 2 | 5 |
| Outlet | 5.5 | 7 | 22 | 5 |

The gas is then passed through two mist eliminator units. The first a chevron above the sieve trays and the second a packed vessel (Tellerette packing) in the duct after the scrubber. The gas is reheated by an afterburner to 140°C in winter and 110°C in summer.

The scrubber effluent, rich in sodium bisulfite, is heated in a double-effect evaporator by steam to crystallize sodium sulfite and to regenerate $SO_2$.

Sodium sulfite is separated by centrifuge, dissolved in water, and returned to the absorber. $SO_2$ gas containing steam is cooled in a condenser to separate water and sent to a sulfuric acid plant. The tail gas from the acid plant is treated by a small auxiliary scrubber for $SO_2$ removal.

The Chubu unit is built almost entirely of stainless steel.

## Water Treatment System

Many pieces of equipment are required for the water treatment. A portion of the sodium sulfite is oxidized in the scrubber by oxygen in the flue gas to form sodium sulfate. A small amount of sodium thiosulfate forms in the evaporator. Neither the sulfate or the thiosulfate can absorb $SO_2$ and must be removed from the liquor. To remove the sulfate, a portion of the liquor from the evaporator feed tank is sent to a crystallizer, and cooled to 0°C to crystallize the sulfate, which is separated from the liquor by a centrifuge. The liquor from the centrifuge is returned to the feed tank. As the sulfate crystals contain a small amount of sodium sulfite and bisulfite, they are dissolved in a purge stream from the liquor from the precooling section of the scrubber and further treated along with a small amount of purge stream from the liquor from the sodium sulfite centrifuge containing the thiosulfate. The mixed liquor is treated with sulfuric acid to decompose the sulfite, bisulfite, and thiosulfate; it is then aerated (the $SO_2$ released is sent to the auxiliary scrubber), oxidized with ozone for further decomposition of the thiosulfate, settled to precipitate solids, neutralized with sodium hydroxide, and then discharged into the sea along with other wastewater from power plants. The chemical oxygen demand (COD) is thus kept below 10 ppm, as required by regulations.

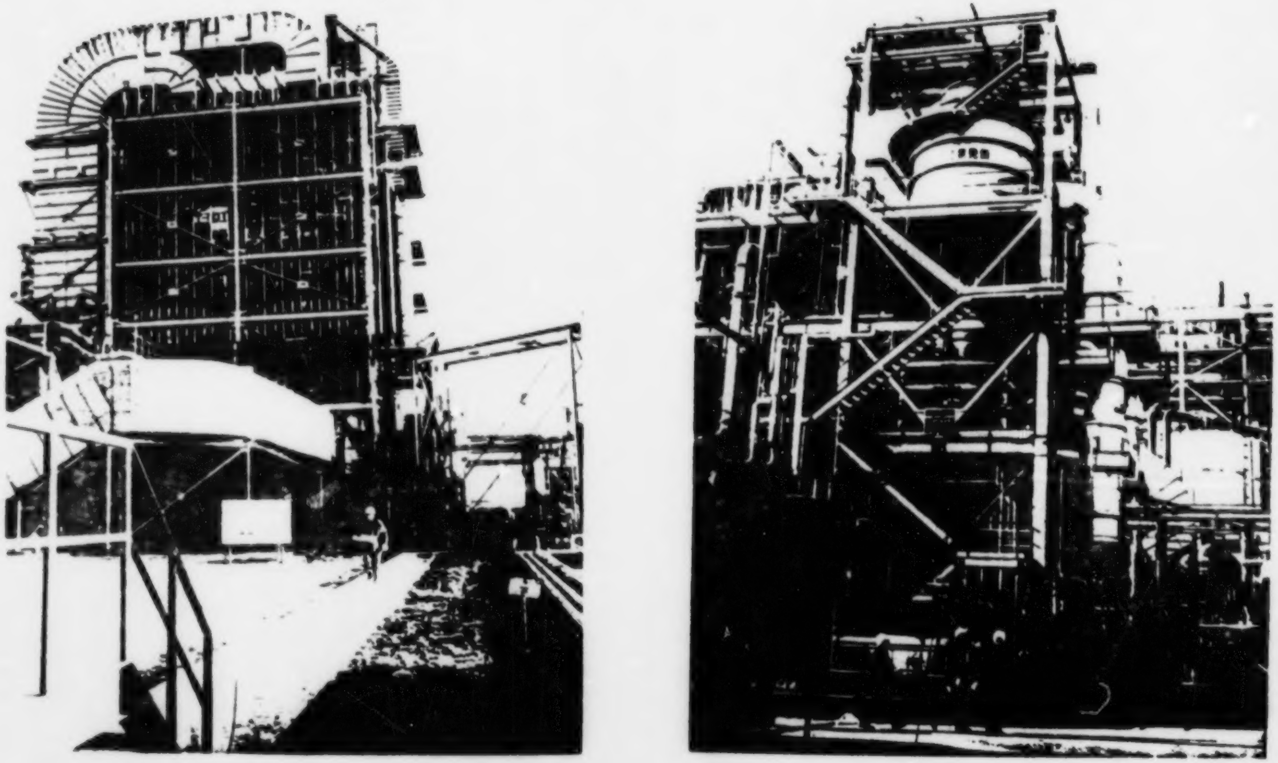
The amount of wastewater from the desulfurization plant is 70 t/day, of which 40 t/day is derived from the purge stream from the precooling section.

MKK does not use an oxidation inhibitor, as does Sumitomo Chemical Engineering Co., to reduce the formation of sodium sulfate, because any oxidation inhibitor would interrupt the abatement of COD in wastewater.

## Performance[9]

The plant was started up in May 1973 (Figure 5-3). At the beginning of the operation a few problems were encountered, such as vibration of the sieve assembly, difficulty in controlling the draft at the ID fan at low load, and high turbidity of the by-product acid. Those problems were solved in a few months, and the plant has been in smooth operation since then. Typical operation data are shown below:

| | |
|---|---|
| Inlet $SO_2$ | 1800 ppm |
| Outlet $SO_2$ | 140 ppm (scrubber outlet) |
| L/G ratio | 0.7 liter/$Nm^3$ (about 5 gal./1000 scf) |
| Pressure drop | 500 mm $H_2O$ (scrubber and mist eliminator) |
| Make-up sodium hydroxide | 7 t/day |



Absorber

Evaporator

Figure 5-3. Nishinagoya plant, Chubu Electric.

| | |
|---|---|
| By-product sulfuric acid | 80 t/day |
| Steam | Total 24 t/hr (19 t/hr for evaporation) |
| Oil for reheating | (0.5 percent S) |
| 2.5 kl/hr for reheating to 140°C | |
| 1.5 kl/hr for reheating to 110°C | |
| Oil for boiler (3 percent S) | 50 kl/hr |

Of the make-up sodium hydroxide (7 t/hr), about half is used to compensate for the loss by sodium sulfate formation and the rest for other losses.

A major feature of the Nishinagoya plant is the expensive and highly automated control system. The main control is for the amount of liquor fed to the scrubber, which is varied to keep a uniform $SO_2$ concentration in the scrubber exit gas; the boiler load is used as an advance signal for changes. Only two operators are required.

The high degree of automation is required because of the widely fluctuating load; the capacity factor is 42 percent and the boiler is shut down every week end. This wide variation makes necessary other control measures in addition to automation. The surge volume after the scrubber was designed to be large enough to allow the evaporator and acid plant to continue operating at minimum load during shutdown of the boiler and main scrubber. The acid plant is difficult to restart if it is shut down. The small auxiliary scrubber has been installed to scrub the acid plant tail gas during such periods.

The liquor is distributed over the sieve trays by a spray system in order to provide good gas-liquid contact even at low gas flow. As the liquor readily flows down the tray when the load falls below 110 MW, the L/G ratio is increased and the liquor feed rate is kept at a minimum of 18 $m^3$/hr to maintain high desulfurization efficiency.

### Evaluation

The Nishinagoya plant is reliable and easy to control. The plant cost, however, is high - about $6 million in 1972-73, including $1 million for the control system. The cost is about 30 percent higher than cost of the wet lime/limestone system. The consumption of sodium hydroxide and steam and the volume of wastewater are also fairly high. If wastewater containing sodium sulfate is not purged, some means will be needed to decompose the sodium sulfate to recover sodium hydroxide.

## ONAHAMA-TSUKISHIMA MAGNESIUM PROCESS[3,8]

### State of Development

Onahama Smelting and Refining Co. jointly with Tsukishima Kikai Co. (TSK) developed a magnesium scrubbing process and constructed a plant at the Onahama Works, Onahama Smelting and Refining Co., with a capacity of treating 90,000 $Nm^3$/hr of waste gas from a reverberatory furnace; the gas contains 15,000 to 25,000 ppm $SO_2$. The plant has been operated since January 1973, by-producing concentrated $SO_2$ gas (10 to 13 percent), which is used for sulfuric acid production.

### Process Description

A simplified flowsheet of the process is shown in Figure 5-4. The waste gas passing through an electrostatic precipitator and cooler is treated in one of two TCA scrubbers, each 4.5 m in diameter and 27 m high, with a magnesium hydroxide slurry. Well-grown crystals of $MgSO_3 \cdot 6H_2O$ are formed by the reaction with $SO_2$ and are easily centrifuged. The sulfite is dried in a special dryer with indirect heating (3 m in diameter, 25 m long) and then calcined in an oil-fired rotary kiln (3.4 m in diameter, 52 m long). Coke is added to reduce magnesium sulfate formed in the scrubber and dryer. The regenerated MgO is slaked and recycled. The kiln off-gas is washed and fed to the acid plant.

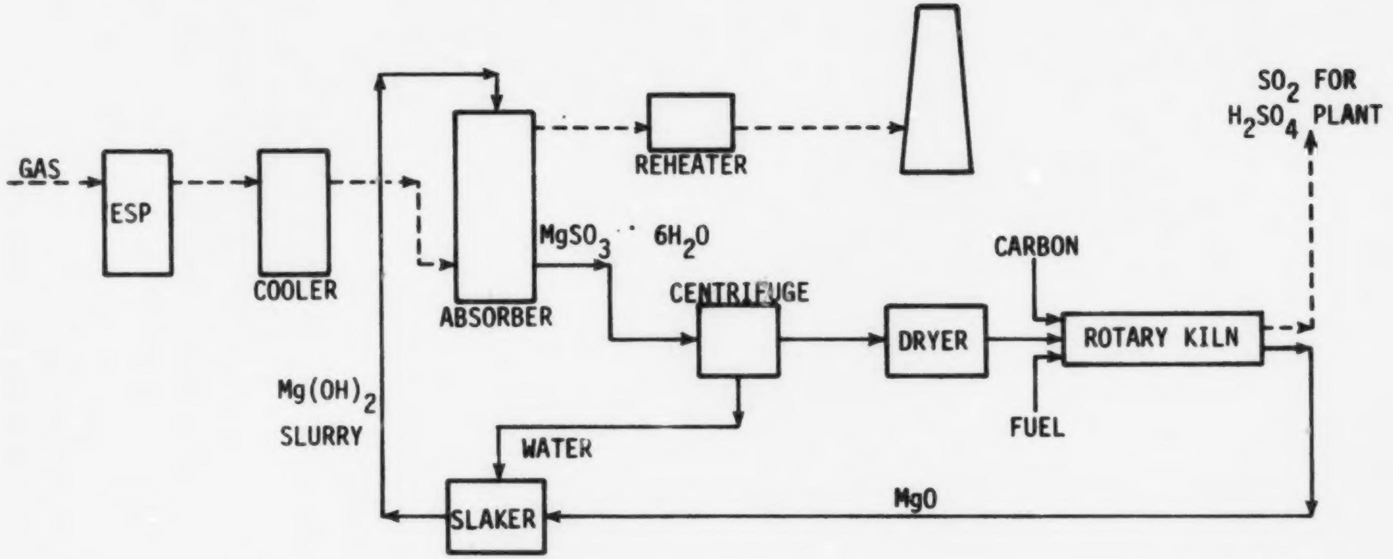

GAS
ESP
COOLER
ABSORBER
REHEATER
$MgSO_3 \cdot 6H_2O$
CENTRIFUGE
DRYER
CARBON
FUEL
ROTARY KILN
$SO_2$ FOR
$H_2SO_4$ PLANT
$Mg(OH)_2$
SLURRY
WATER
SLAKER
MgO

Figure 5-4. Simplified flowsheet of Onahama-Tsukishima process.

## Performance

$SO_2$ in the waste gas is reduced from 15,000 to 25,000 ppm to less than 100 ppm; the removal efficiency is better than 99.5 percent. The main problem with the process has been scaling on the scrubber walls due to the crystallization of magnesium sulfite. The current practice is to use two scrubbers alternately every two weeks or so and remove the scale by washing with sulfuric acid. Since installation of the extra scrubber, overall system availability has been good. Ball wear has also been a problem, necessitating replacement every few months. The balls are made of polyethylene.

Centrifuge and dryer operation has been trouble-free. Oxidation in the system is about 10 percent. The coke gives adequate reduction; the concentration of $MgSO_4$ in MgO from the kiln is less than 1 percent. Some larger agglomerates of MgO, formed during the calcination, are ground for slaking. Steam consumption is not more than 0.13 t/t $SO_2$, and MgO make-up is less than 0.08 t/t $SO_2$. The loss of MgO is caused mainly by MgO dust in the kiln gas, which is washed before passing to the sulfuric acid plant. Consideration is being given to recovery of the MgO.

## Evaluation

The whole system is working well except for the scaling in the scrubber. The scaling may be caused by the very high $SO_2$ concentration and may not be a problem for usual flue gas treatment. For treating such concentrated gas, the TCA scrubber may not be the best choice. With some improvement, the process may be very useful, particularly for plants that need sulfuric acid.

## OTHER WET PROCESSES

### Sodium Scrubbing Processes By-Producing Sodium Sulfite or Sulfate

More than 100 sodium scrubbing units in Japan yield sodium sulfite or sulfate as by-products. Most have capacities of 10,000 to 150,000 $Nm^3$/hr (the largest one is 300,000 $Nm^3$/hr) and treat gases from oil-fired and Kraft recovery boilers, sulfuric acid plants, glass smelting furnaces, and similar operations. Various types of scrubbers are used to recover 90 percent or more of the $SO_2$. Major constructors are Oji and Kurabo (Table 2-5).

In most plants, $SO_2$ is absorbed with a sodium sulfite solution to give a sodium bisulfite solution, which is then neutralized with sodium hydroxide to produce the sulfite. A portion of the sulfite solution is returned to the scrubber and the rest is sold to paper mills in the form of solution or crystal. Usually sodium hydroxide solution is not used directly for flue gas treatment because it also absorbs $CO_2$.

Hitachi Ltd. has developed a semi-wet process that uses sodium hydroxide solution directly for flue gas treatment. The solution is sprayed from the top of a tower to which a flue gas is introduced at about 170°C . A powdery product containing sodium sulfite (about 60 percent), sulfate, and carbonate (about 20 percent each) is formed and is caught by dust collectors. The product can be used for Kraft pulp production. A few commercial units based on this process have been constructed.

In about 20 units the sodium sulfite is oxidized into sulfate by bubbling air into the solution. The sulfate is either purged or recovered as crystal to be used in glass manufacture and other industries.

### Wellman-SCEC Process

Sumitomo Chemical Engineering Co. (SCEC) has constructed several plants using the Wellman-Lord process, as shown in Table 5-1. The SCEC process is similar to the Wellman-MKK process except that SCEC uses a sodium sulfite centrifuge and an oxidation inhibitor. The inhibitor depresses the oxidation of the sulfite into sulfate to less than half but also affects the oxidation of reducing compounds in wastewater. Still, the COD of wastewater can be reduced to below 20 ppm, as required by local regulations.

The recovered $SO_2$ is used in various ways: it is returned to a Claus furnace at the Kawasaki plant, Toa Nenryo; used for sulfuric acid production at the Chiba plant, Sumitomo Chiba Chemical; and used as liquid $SO_2$ at the Fuji plant, Fuji Film Co., which went into operation a few months ago. In addition to the plants listed in Table 5-1, a unit is under construction at Wakayama Refinery, Toa Nenryo, to treat 20,000 $Nm^3$/hr of tail gas from a Claus furnace to recover $SO_2$, which will be returned to the Claus furnace.

## Magnesium Scrubbing Processes

In addition to the Onahama-Tsukishima process, two other magnesium scrubbing processes are being used commercially. Mitsui Mining and Smelting Co. in 1971 constructed at Hibi Works a unit treating tail gas (80,000 $Nm^3$/hr; 1500 to 2000 ppm $SO_2$) from a sulfuric acid plant using its own process.[3] A cross-flow-type absorber is used, and $MgSO_3 \cdot 6H_2O$ is formed. The sulfite crystal is separated by a centrifuge from the solution, which contains some magnesium sulfate formed by oxidation. The sulfite is dried in a rotary dryer and then calcined in an indirect calciner at 750°C. The regenerated $SO_2$ is returned to the acid plant. The magnesium sulfate solution is concentrated to produce $MgSO_4 \cdot 7H_2O$, which is sold for fertilizer and other uses.

Mitsui Miike Machinery Co. recently constructed for Idemitsu Kosan (Chiba refinery) a Chemico-process plant with a capacity of treating 500,000 $Nm^3$/hr of tail gas from a Claus furnace. The plant went into operation in November 1974. No details of operation have yet been disclosed.

Mitsui Shipbuilding Co. constructed a pilot plant using the Grillo process (magnesium manganese scrubbing) as previously reported.[3] There has been no notable development since.

## Ammonia Scrubbing - IFP Process

Mitsubishi Heavy Industries has constructed a plant with a capacity of treating 27,000 $Nm^3$/hr of tail gas from a Claus furnace for Maruzen Oil Co. at Shimozu refinery. The system incorporates ammonia scrubbing and thermal decomposition with the IFP process to produce elemental sulfur.[3] The plant went into operation early in 1974 but has had many problems. Several modifications have been made for improvement.

Toyo Engineering constructed a similar plant (6000 $Nm^3$/hr, for Fuji Oil Co. at Chiba refinery), which went into operation in June 1974 (Figure 5-5). This plant also has encountered many problems and is now under modification.

The ammonia scrubbing - IFP process is not simple and plant operation apparently is not easy. Capacity may be limited because of the limited size of the submerged combustion unit.

## Tsukishima Sulfix Process

Tsukishima Kikai Co. (TSK) has been licensed by SCA of Sweden for the Billerud process, designed to reduce sodium sulfite in waste liquors by injecting the liquor into an oil burner operating under partial oxidation conditions. TSK has recently performed pilot plant work on adapting the Billerud process to reduction of sodium sulfite obtained from sodium scrubbing of waste gas (Figure 5-6). Sodium sulfite solution from the scrubber is reduced in the reactor and the resulting sodium carbonate is collected in an electrostatic precipitator. The reactor effluent gas containing 4 to 7 percent $H_2S$ is sent to a Claus furnace or treated by the Takahax process[3] to convert $H_2S$ into sulfur. There is no plan yet to build a commercial plant.

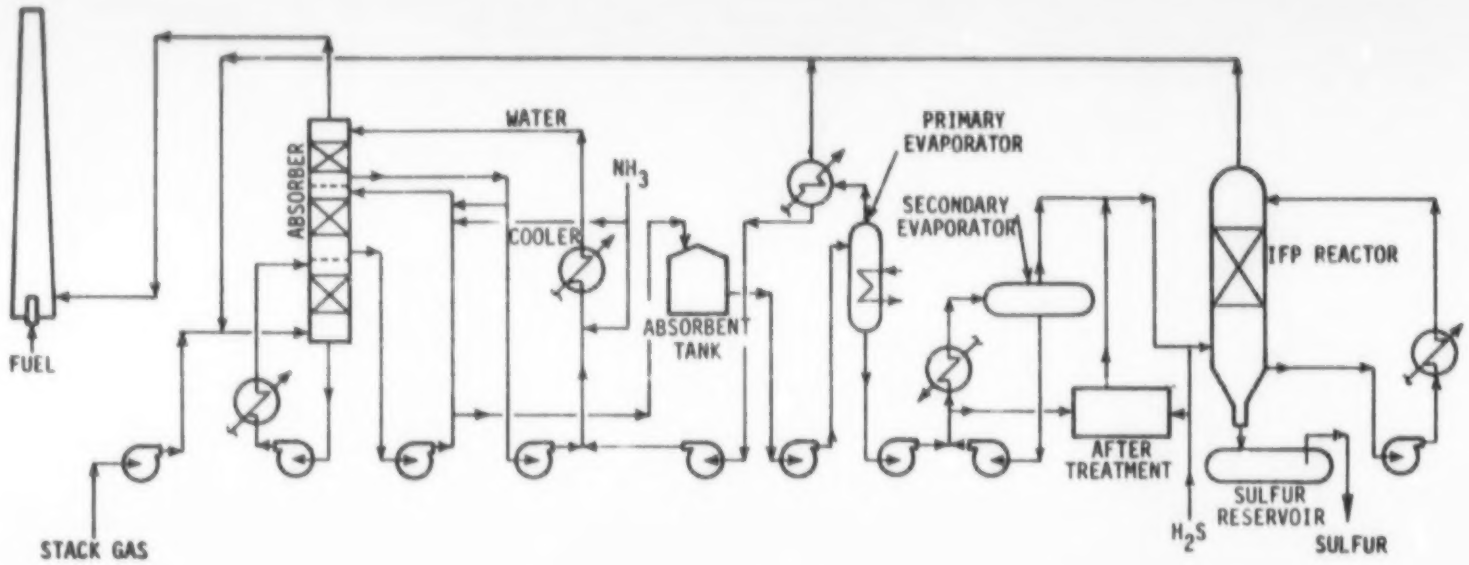

WATER
NH$_3$
PRIMARY EVAPORATOR
SECONDARY EVAPORATOR
ABSORBER
COOLER
ABSORBENT TANK
IFP REACTOR
FUEL
STACK GAS
AFTER TREATMENT
H$_2$S
SULFUR RESERVOIR
SULFUR

Figure 5-5. Flowsheet of IFP process offered by Toyo Engineering.

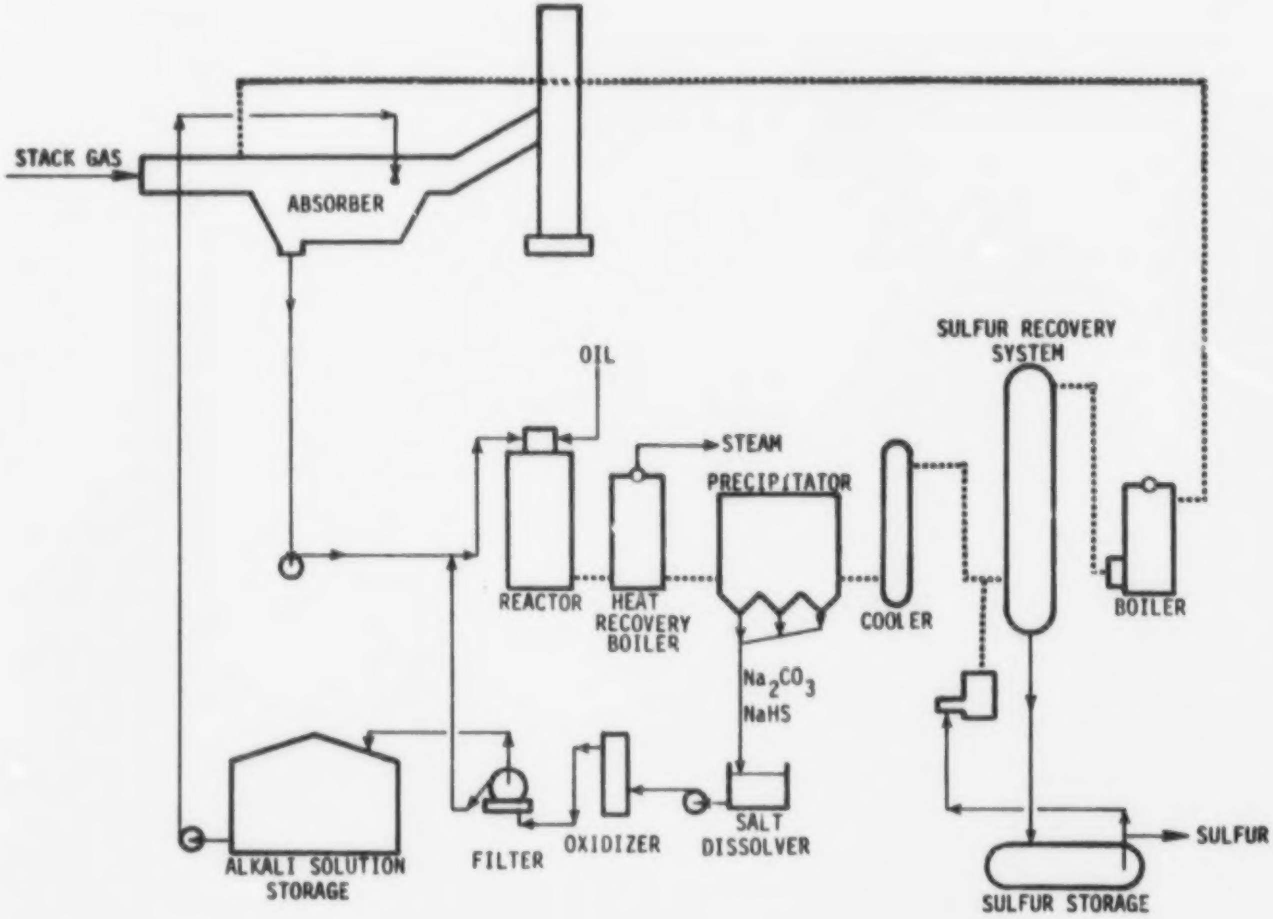

STACK GAS
ABSORBER
OIL
STEAM
SULFUR RECOVERY SYSTEM
PRECIPITATOR
REACTOR
HEAT RECOVERY BOILER
COOLER
BOILER
$Na_2CO_3$
NaHS
ALKALI SOLUTION STORAGE
FILTER
OXIDIZER
SALT DISSOLVER
SULFUR
SULFUR STORAGE

Figure 5-6. Flowsheet of TSK Sulfix process.

## SHELL COPPER OXIDE PROCESS

### State of Development

This process has been developed by the Shell group, Netherlands. Shell built a pilot plant at Pernis (1000 $Nm^3/hr$) in 1967 and has operated it for over 20,000 hours. Japan Shell Technology Co. (2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo) has been the licensor of the process in the Far East. The first commercial plant, with a capacity of treating 125,000 $Nm^3/hr$ of flue gas from an oil-fired boiler, was constructed at Yokkaichi refinery, Showa Yokkaichi Sekiyu (SYS) (Figure 5-7). The plant went into operation in August 1973 by-producing concentrated $SO_2$ gas, which is sent to a Claus furnace for elemental sulfur production.

### Process Description[11,12]

The flowsheet of the process at SYS is shown in Figure 5-8. Flue gas at 400°C containing 1300 ppm $SO_2$ flows into one of two parallel reactors (Figure 5-9), where about 90 percent of the $SO_2$ is absorbed by CuO (impregnated into alumina granules) to form $CuSO_4$. After about 90 minutes "acceptance flow," the gas is shifted to the other reactor. Steam is introduced into the first reactor for a short time to purge the flue gas, and then a reducing gas (hydrogen at SYS) is passed through the reactor, producing a regeneration off-gas that contains $SO_2$, steam, some hydrogen and inert matter. The $CuSO_4$ is reduced to copper metal in this regeneration step. After the regeneration is over, steam is introduced again to purge hydrogen prior to the introduction of flue gas. The total time of the hydrogen and steam injections is equal to that of the flue gas injection and thus the two reactors serve as "acceptor" and "regenerator" alternately. One cycle takes about 3 hours. The metallic copper formed in the regeneration step is immediately oxidized in an early stage of acceptance by oxygen in the flue gas. Therefore, the actual accepting material is CuO.

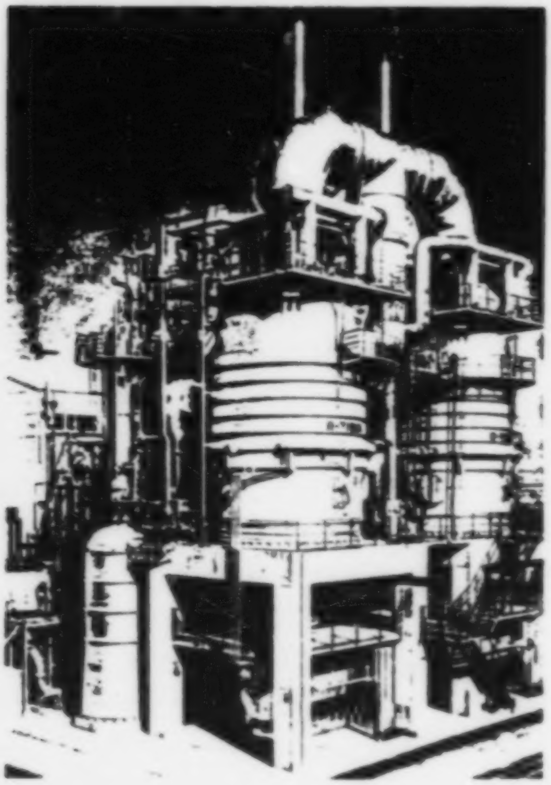
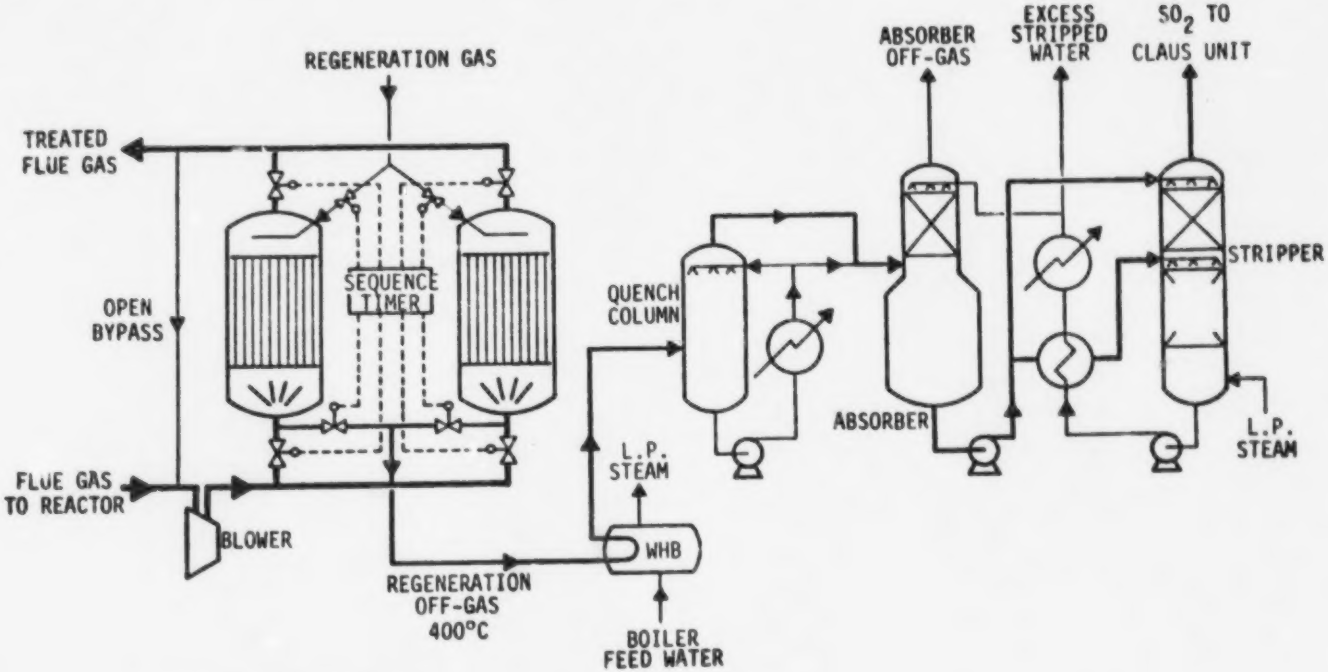


Figure 5-7. Yokkaichi plant, SYS (Shell process).


REGENERATION GAS
TREATED FLUE GAS
OPEN BYPASS
FLUE GAS TO REACTOR
BLOWER
SEQUENCE TIMER
REGENERATION OFF-GAS 400°C
L.P. STEAM
WHB
BOILER FEED WATER
QUENCH COLUMN
ABSORBER OFF-GAS
ABSORBER
EXCESS STRIPPED WATER
SO2 TO CLAUS UNIT
STRIPPER
L.P. STEAM

ACCEPTANCE TIME: 120 min.

Figure 5-8. Flowsheet of Shell process (Yokkaichi plant, SYS).

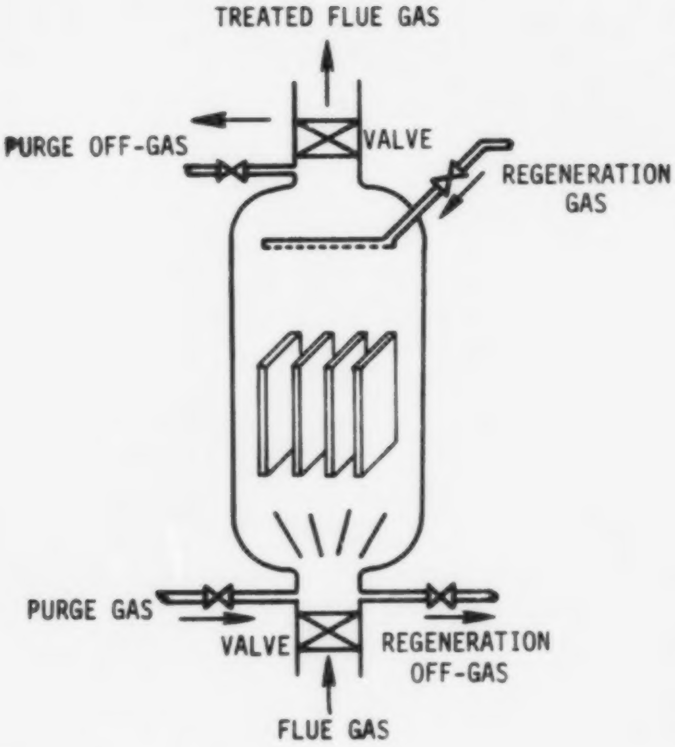

TREATED FLUE GAS
PURGE OFF-GAS
VALVE
REGENERATION GAS
PURGE GAS
VALVE
REGENERATION OFF-GAS
FLUE GAS

Figure 5-9. Reactor
(Shell process).

Because the $SO_2$ flow rate from the regenerator varies from nil to maximum every 90 minutes, a wet-type absorber-stripper system is installed to produce a uniform flow to the Claus furnace. The regenerator off-gas is passed through a waste-heat boiler and a quench column and then introduced into the absorber. In the absorber, $SO_2$ is absorbed in water under some pressure. More than 99.5 percent of the $SO_2$ is recovered. The absorber off-gas containing hydrogen, hydrocarbons, and a little $SO_2$ is sent to the boiler for burning and $SO_2$ recovery. The liquor discharged from the absorber is sent to the stripper to release $SO_2$, which is sent to the Claus furnace.

## Performance

The SYS unit encountered a few problems after its start-up in August 1973. The problems included corrosion of the quench column and sticking of PRC valve on a hydrogen by-pass line; both have been solved. Another problem has been plugging of the waste-heat boiler tubes due to the deposit of ferrous sulfate formed by corrosion of carbon steel by regenerated $SO_2$. The plugging may be eliminated by the use of stainless steel.

The unit underwent the thousandth cycle in January 1975, an indication that net operation reached 3000 hours. The copper acceptor has shown a slight decrease in activity, but since the $SO_2$ recovery is still satisfactory - nearly 90 percent - the acceptor can be used for many more cycles.

Precautions have been taken to eliminate any danger that could occur from the use of hydrogen. For example, the hydrogen is diluted so that the gas has no explosive potential even when mixed with some flue gas. The vessels are designed to resist a considerable pressure, which might be produced in case hydrogen is burned. Neither explosion nor burning has been experienced.

Steam is injected to the stripper, from which a considerable amount of wastewater containing 20 to 40 ppm (weight) sulfur compounds is discharged. Hydrogen consumption runs to 0.19 to 0.20 kg/kg S recovered.

Evaluation

The reactors are smaller than those of dry carbon absorption processes with an equal capacity, indicating the high reactivity of the copper acceptor. The wet absorber-stripper may be a drawback for other installations, however, since the stripper requires a considerable amount of steam and produces wastewater. The water must be treated before being used for some purpose, for example, as a boiler feed. There may be other ways to work up the $SO_2$ regenerated. In a larger plant with several reactors, it may be possible to eliminate the absorber-stripper system.

The Shell process may not be suitable for existing boilers with normal flue gas temperatures of 120 to 150°C, because the gas must be heated to 400°C. For a new power plant, the unit may be installed between the boiler and the air preheater to reduce the required temperature adjustment. A high-efficiency hot electrostatic precipitator, which may be fairly expensive, will be required in this case. On the other hand, the treated flue gas may be cooled in an air preheater to as low as 100°C because the flue gas is free from $SO_3$, and thus a considerable energy saving, about 1.5 percent of the fuel input to the boiler, will be achieved.

Another point to be considered in applying the process to utility boilers is the fluctuation of the operating load. Although a hydrogen production plant may be able to change the operating load, it may be difficult for the plant to follow the variation of the boiler load.

Two years ago the capital cost of the SYS plant was ¥ 1.0 billion ($3.3 million), excluding the hydrogen plant and Claus furnace, which are part of other refinery facilities. The process is more expensive than the wet-lime process but has the advantages of requiring no reheating and of producing sulfur. Moreover, the Shell process may have a capability for simultaneous removal of $NO_x$ and $SO_x$ by ammonia injection into the acceptor, because copper oxide can act as a catalyst for the reaction of $NO_x$ and ammonia to form nitrogen.

## OTHER DRY PROCESSES

### Carbon Processes

Sumitomo Shipbuilding and Machinery Co. constructed a carbon absorption plant with a capacity of treating 175,000 $Nm^3$/hr of flue gas from an oil-fired boiler for Kansai Electric at its Sakai Station.[3] $SO_2$ is absorbed by moving beds of activated carbon. After the $SO_2$ absorption, the carbon is heated again in moving beds by an inert gas to release $SO_2$, which is used for sulfuric acid production. The plant has been operated smoothly since 1972.

Hitachi Ltd. constructed a carbon process plant for Tokyo Electric Power. This plant also has been operated well. But there is no plan to build a new plant with either the Hitachi or the Sumitomo process, possibly because of the high investment cost and the difficulty of attaining $SO_2$ recovery of more than 90 percent. Hitachi Shipbuilding has given up the development of a carbon process using heated steam for regeneration.[3]

### Mitsubishi Manganese Process

Mitsubishi Heavy Industries constructed a dry manganese process plant for Chubu Electric Power at its Yokkaichi Station. The plant has a capacity of treating 400,000 $Nm^3$/hr of flue gas from an oil-fired boiler and came on-stream in 1972. Operation and further development of the process were given up recently, possibly because of the economic disadvantages and the difficulty of attaining more than 90 percent $SO_2$ recovery.

## Hitachi Shipbuilding Reduction Process

National Research Institute of Pollution and Resources is working on a process for $SO_2$ absorption with powdered sodium carbonate followed by decomposition of the product sodium sulfate by a reducing gas to produce $H_2S$.[3] There has been no recent progress.

# 6. BY-PRODUCTS

## INTRODUCTION

Recently in Japan about 6 million tons yearly of $SO_2$ have been emitted, mainly by the burning of heavy fuel oil. Desulfurization efforts have been made in earnest since 1966. Among various desulfurization processes, those which first became popular were hydrodesulfurization of heavy oil, by-producing elemental sulfur, and sodium scrubbing of waste gases, by-producing sodium sulfite (Figure 6-1). A wet lime process plant that by-produces salable gypsum has been in operation since 1964 but not until 1972 was construction started on many plants by-producing gypsum. Processes that give by-product sulfuric acid, elemental sulfur, and calcium sulfite have been developed since 1971. The discarding of calcium sulfite sludge is not as widespread in Japan as it is in the United States because of limitations on land available for disposal.

Since many desulfurization plants are to be built, it is likely that in the future the supply of by-products will far exceed the demand and that a substantial portion of them will have to be discarded. Gypsum is generally considered the most reasonable by-product because the demand for it is increasing and because it can be discarded easily. The various by-products from waste gas desulfurization processes are discussed in the remainder of this section.

### Sodium Sulfite

The author has reported earlier on the sodium scrubbing processes by-producing sodium salts. The reasons for the rapid development of the processes are their simplicity and

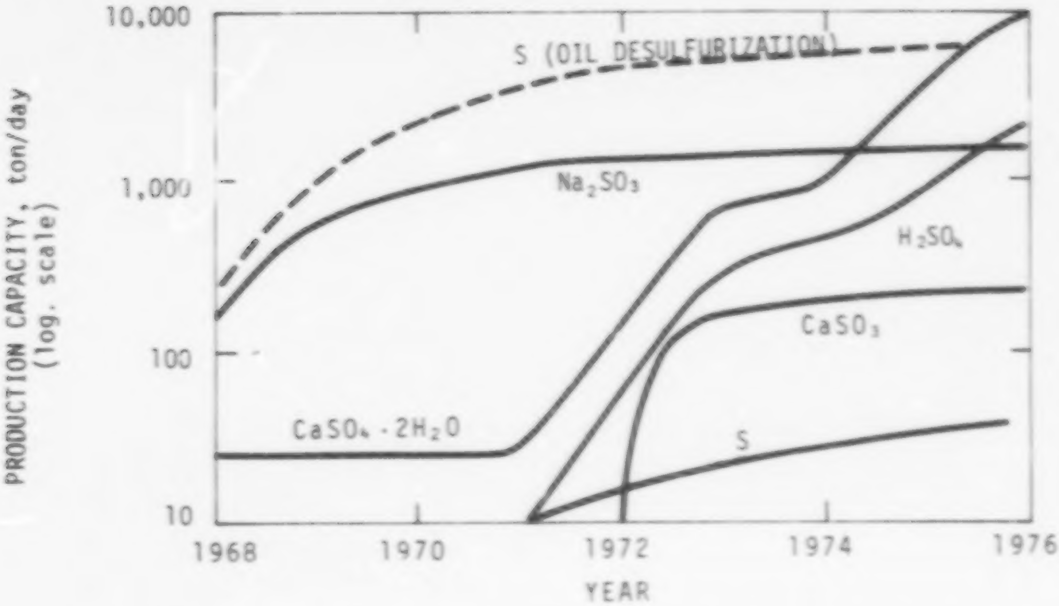


Figure 6-1. By-production capacity of waste gas desulfurization.

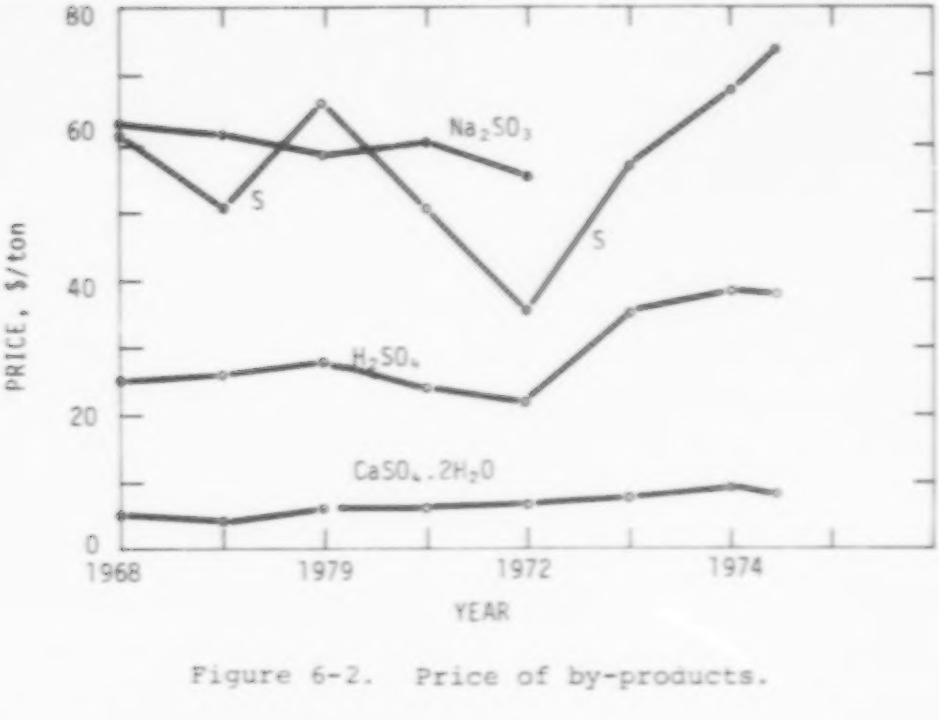


Figure 6-2. Price of by-products.

the usefulness of the by-product sodium sulfite for paper mills. More than 100 plants have been installed, mainly to treat effluents from relatively small gas sources, industrial boilers, and chemical plants. Yearly production of sodium sulfite has reached 320,000 tons and has already filled the demand and caused a decrease in the selling price (Figure 6-2). Nevertheless, the $SO_2$ recovered as sulfite is only 4 percent of the total emission. Asahi Glass Co. recovers $SO_2$ from a glass furnace to produce sodium sulfite, which is oxidized into sulfate and returned to the furnace. There is not much demand for sodium sulfate, either. Several smaller plants produce waste sodium sulfite or sulfate solution. Not many additional sodium scrubbing plants are expected to be built in the future.

## SULFURIC ACID

The sources and uses of sulfuric acid in Japan are listed in Table 6-1. Pyrite, which was the major source of the acid, has been gradually replaced by smelter gas and sulfur. Production of the acid by flue gas desulfurization was begun in 1971. The production capacity is expected to reach 900 tons/day in 1975. But continuing rapid development cannot be expected because the increase in the demand is only 200,000 to 300,000 tons yearly.

The Wellman-Lord process has been the major process for production of sulfuric acid. At present, five plants are in operation that use the process and seven are under construction. The sulfuric acid production capacity of those plants will reach 760 tons/day by the end of 1975.

An $SO_2$ recovery plant using the Sumitomo activated-carbon process has been in operation at the Sakai Power Station of Kansai Electric, treating 150,000 $Nm^3/hr$ of flue gas from an oil-fired utility boiler. One advantage in producing sulfuric acid from the recovered $SO_2$ by the Wellman-Lord and Sumitomo processes is that the vessels used for

Table 6-1. SOURCES AND USES OF SULFURIC ACID IN JAPAN
(thousands of tons)

| Source | 1971 | 1972 | 1973 |
|---|---|---|---|
| Smelter gas | 3,120 | 3,783 | 4,310 |
| Pyrite | 3,260 | 2,340 | 1,692 |
| Sulfur | 130 | 398 | 855 |
| Others | 65 | 126 | 148 |
| Total | 6,575 | 6,647 | 7,005 |
| Use | | | |
| Fertilizer | 2,176 | 2,321 | 2,304 |
| Others | 4,429 | 4,486 | 4,736 |
| Total | 6,605 | 6,807 | 7,040 |

producing the acid are small because of the high $SO_2$ concentration of the gas to be fed into the acid plant--nearly 100 percent for Wellman and 10 to 20 percent for Sumitomo, as compared with 6 to 10 percent for the gas produced by pyrite or sulfur burning. There is no plan, however, to install a larger carbon process plant.

Two magnesium scrubbing plants are in operation using the Mitsui Mining process and the Onahama-Tsukishima process. Both are installed in copper smelters with sulfuric acid plants. The former treats 75,000 $Nm^3$/hr of tail gas from a sulfuric acid plant and the latter 84,000 $Nm^3$/hr of converter gas containing 2 percent $SO_2$. The recovered $SO_2$ is sent to sulfuric acid plants.

## ELEMENTAL SULFUR

Recently in Japan the supply of elemental sulfur has been provided mainly as the by-product from hydrodesulfurization of heavy oil (Table 6-2).

Table 6-2. SUPPLY OF AND DEMAND FOR SULFUR (thousands of tons)

| | | 1972 | 1973 | 1974 (estimate) |
|---|---|---|---|---|
| Supply | Mined | 11 | 0 | 0 |
| | Recovered | 560 | 685 | 792 |
| | Imported | 12 | 59 | 59 |
| | Total | 583 | 744 | 851 |
| Demand | Domestic | 545 | 678 | 752 |
| | Export | 48 | 56 | 57 |

Four processes are currently producing sulfur as a by-product of waste gas desulfurization: (1) the Wellman-Lord process with a Claus furnace; (2) the Shell process with a Claus furnace; (3) ammonia scrubbing with an IFP reactor, and (4) magnesia scrubbing with a Claus furnace. A plant with process (1) has been in operation since 1971 at the Kawasaki plant of Toa Nenryo, treating tail gas (66,000 $Nm^3/hr$) from a Claus furnace; the gas contains 6000 ppm $SO_2$. Two plants using processes (2) and (3) have started operation recently; the Shell process is used at the Yokkaichi plant of Showa Yokkaichi Oil, treating flue gas (110,000 $Nm^3/hr$) from an oil-fired industrial boiler, and ammonia scrubbing is used at the Shimozu plant of Maruzen Oil, treating tail gas (41,000 $Nm^3/hr$) from a Claus furnace. A plant with process (4) started operation recently at the Chiba plant of Idemitsu Kosan, to treat 468,000 $Nm^3/hr$ tail gas from a Claus furnace and an industrial boiler. The recovery of $SO_2$ from tail gas of the Claus furnace to return to the furnace may be achieved fairly economically, but the by-production of sulfur at power plants would be costly. The sulfur by-producing processes will be further developed when the oversupply of other by-products becomes obvious.

Elemental sulfur has also been recoverd by hydrogen sulfide recovery processes. The Takahax process yields a fine powder of sulfur, intended for use in agricultural chemicals.[3] Not many new uses for sulfur have been studied in Japan, as they have been in the U.S.A.

## AMMONIUM SULFATE

Ammonium sulfate was produced until recently at the Yokkaichi Plant of Chubu Electric using the Mitsubishi manganese process. The plant discontinued operation recently because of the difficulty of removing more than 90 percent of the $SO_2$ in the flue gas and the economical disadvantage.

Until a few years ago there were several ammonia scrubbing plants treating tail gas from sulfuric acid plants to by-produce ammonium sulfate. All of the plants were shut down because of the oversupply of ammonium sulfate. Now there are a few small ammonia scrubbing plants treating flue gas to produce a dilute ammonium sulfate solution to be discarded. The discarding of ammonium sulfate solution is to be restricted because it can cause a eutrophication problem. Because of the present shortage of nitrogen fertilizers in developing countries, a few companies are now considering building ammonium scrubbing plants to by-produce ammonium sulfate for export. Nippon Kokan has developed a process by which $SO_2$ in waste gas and ammonia in coke-oven gas are both recovered to produce ammonium sulfate and has started construction of two large units. There is some doubt, however, as to whether a market for ammonium sulfate can be secured until several years from now.

## CALCIUM SULFITE

Not much calcium sulfite has been produced in Japan because of limitations on its use and on landspace for discarding it. Mitsui Aluminum Co., which has produced calcium sulfite sludge since 1972, is going to use the gypsum production process for new installations because of the poor properties of the sludge. There is no focus on sludge stabilization, as there is in the U.S.A.

The calcium sulfite obtained by the wet-lime processes usually consists of very small crystals about 0.1 micron thick and about 1 micron long; the material is not easy to filter. Calcium sulfite from the sodium-limestone processes of Showa Denko and Kureha-Kawasaki grows into much larger crystals about 1 micron thick and 10 to 30 microns long. At the Saganoseki Smelter of Nippon Mining Co., the sulfite obtained by the Showa Denko process is filtered by a vacuum filter, mixed with copper ore, and fed into a smelter for recovery of $SO_2$. For discarding, the sulfite produced by the sodium-limestone process might be better than that from the wet-lime process.

Lion Fat and Oil Co., jointly with Idemitsu Kosan, has recently produced a synthetic paper from fairly pure calcium sulfite and polyethylene, at a weight ratio of about 70:30. This new product has some defects and is now undergoing improvement.

## GYPSUM

### Marketing of Gypsum

Most of the big $SO_2$ recovery plants now under construction or being planned are oriented toward the by-production of gypsum for the following reasons: (1) Japan has plenty of limestone. (2) The value of other by-products, such as sodium salts, sulfuric acid, and ammonium sulfate, will not increase much since they are already in oversupply. (3) Production of elemental sulfur from $SO_2$ in waste gases is not easy. (4) Japan has little available land on which to dump calcium sulfite sludge. (5) Demand for gypsum has been increasing considerably. (6) Gypsum is suitable for discarding in case of oversupply.

The demand for and supply of gypsum in Japan is illustrated in Figure 6-3. All of the by-product gypsum has been used so far for wallboard production and as a retarder for cement setting because there has been a slight shortage of gypsum in Japan since 1971. But since so many desulfurization plants by-producing gypsum are to be installed, oversupply of gypsum is considered likely to occur in the future. Even at present there is a tendency toward oversupply because of a sharp decrease in wallboard production caused by a current slump in housing construction.

### Use of Gypsum for Wallboard and Cement

For wallboard production, gypsum of an appropriate crystal size (longer than about 30 microns, thicker than about 10 microns) and purity are favored. Gypsum obtained from oil-fired flue gas and from most other gases usually meets these requirements (Figure 6-4).

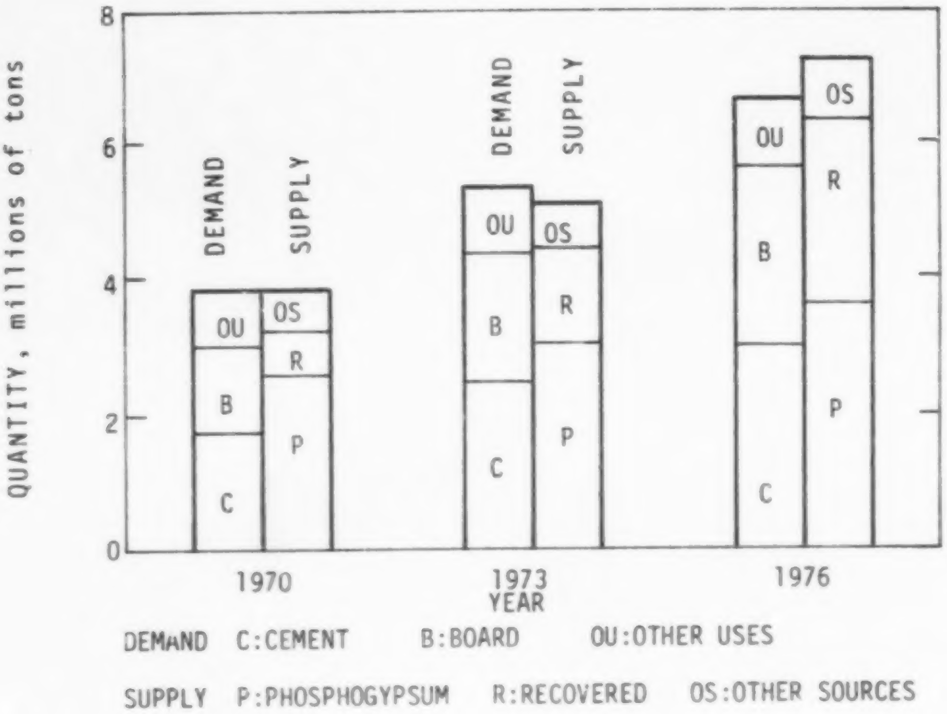
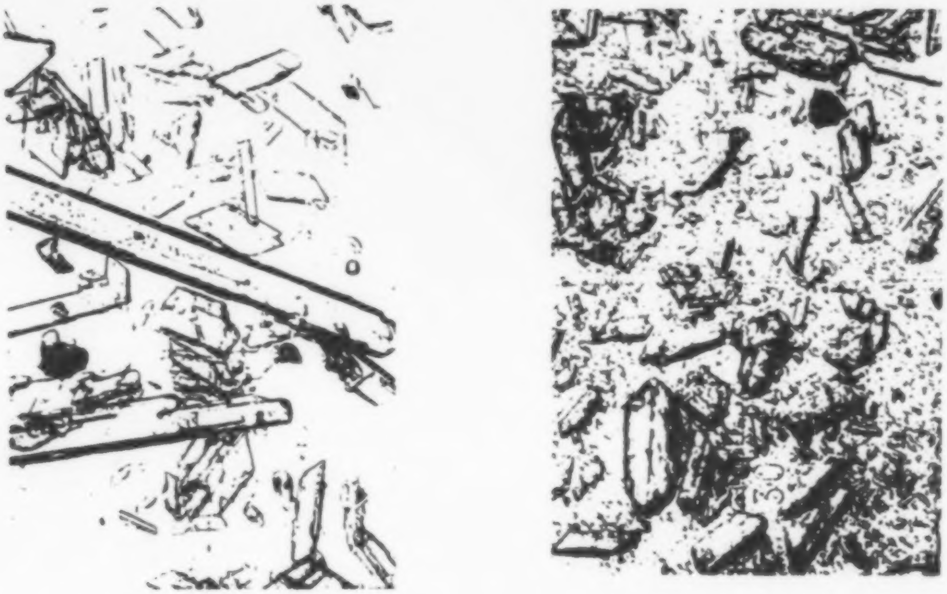
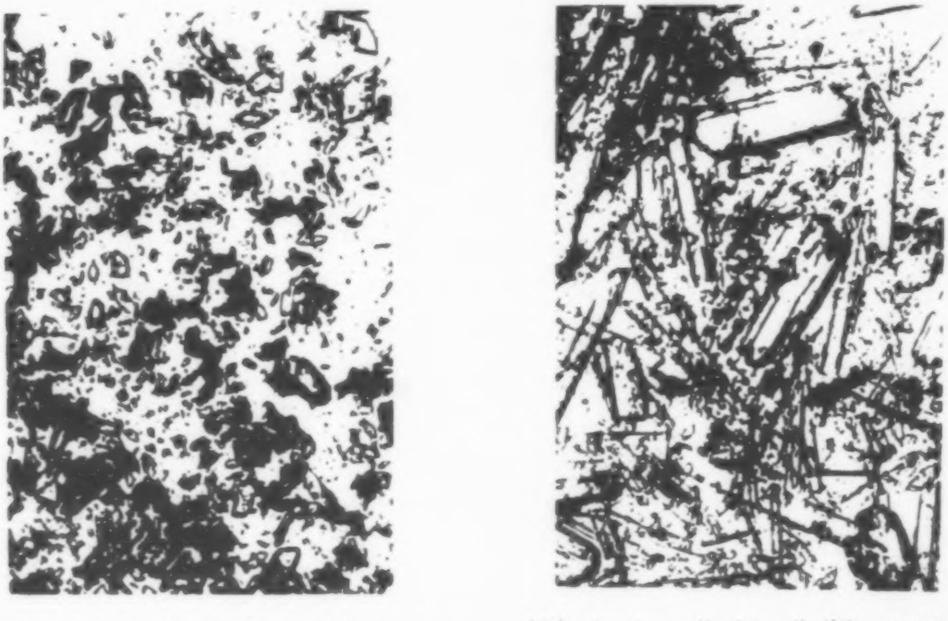


Figure 6-3. Demand for and supply of gypsum in Japan.



(M) $H_2SO_4$-$CaCO_3$ process(Chiyoda, Hokuriku Electric, Toyama)

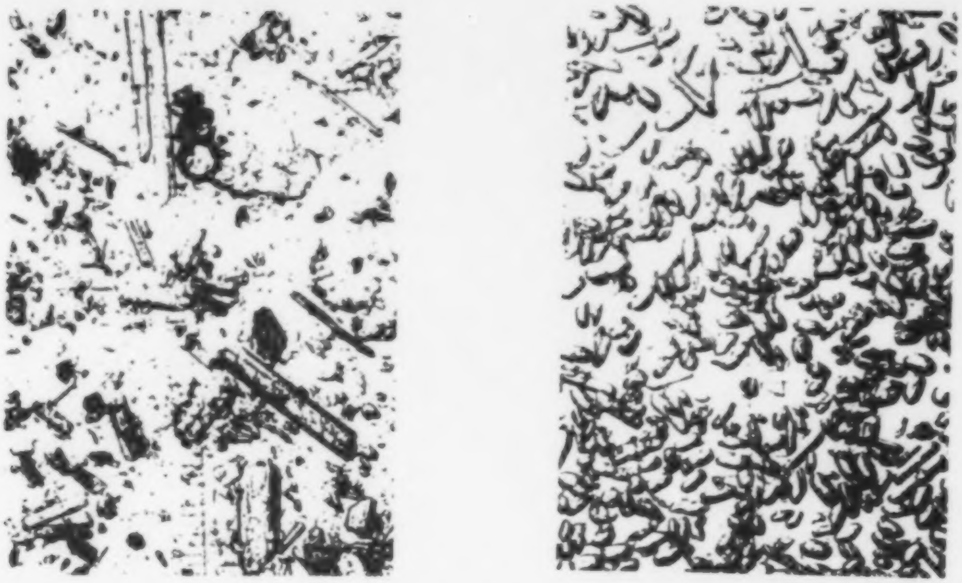
(N) $H_2SO_4$-$CaCO_3$ process (Chiyoda,Daicel,Aboshi)



(O) $Al_2(SO_4)_3$-$CaCO_3$ process (Dowa, Okayama)

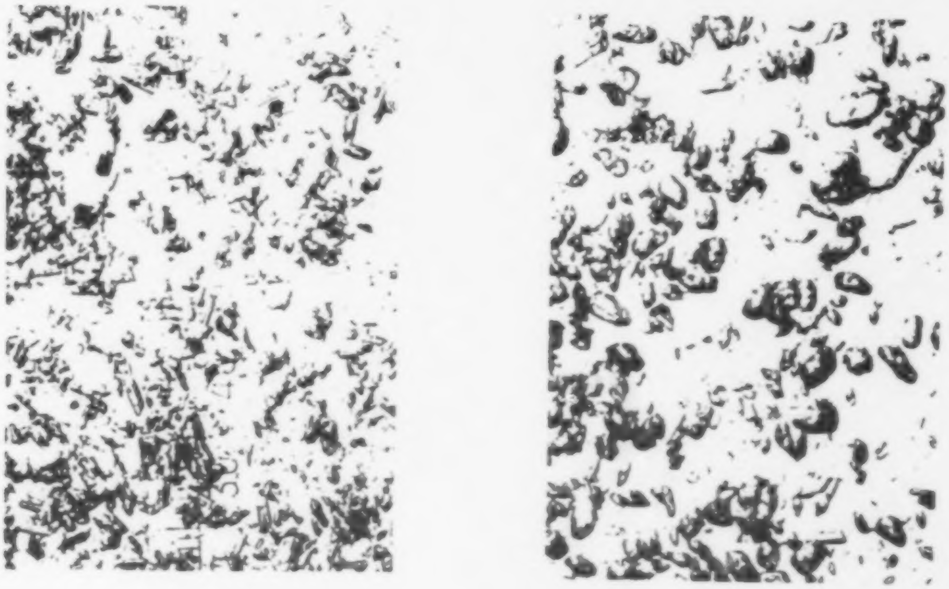
(P) Carbon-$H_2SO_4$-$CaCO_3$ process (Hitachi-Tokyo Electric) (Kashima)

Figure 6-4. Photomicrograms of by-product gypsum (x100).



(E) $Ca(OH)_2$ scrubbing (Mitsubishi-JECCO, Onahama)

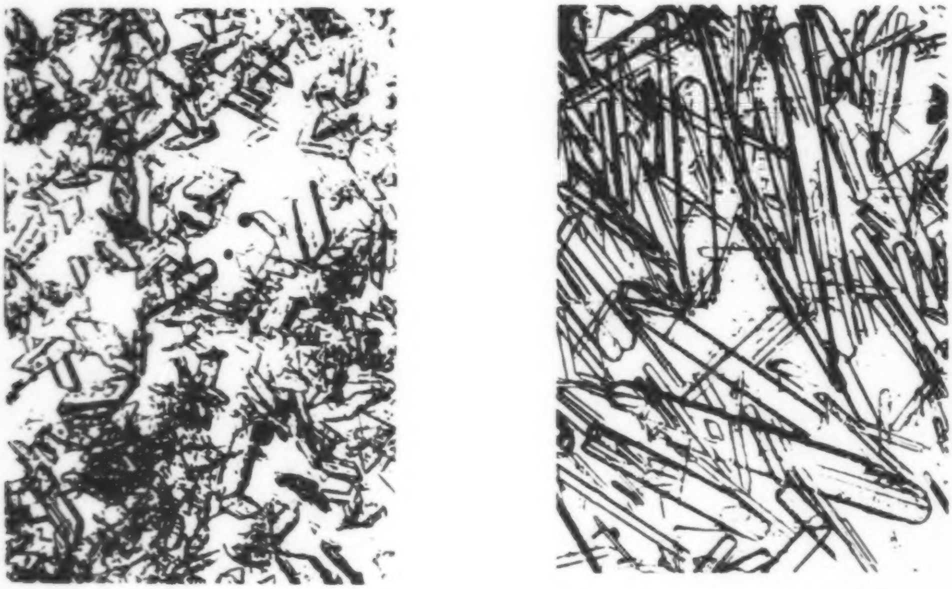
(F) $CaCO_3$ scrubbing(Mitsubishi-JECCO, Tokyo Electric, Yokosuka)



(G) $Ca(OH)_2$ scrubbing (Sumitomo-Fuji Kasui , Sumitomo Metal)

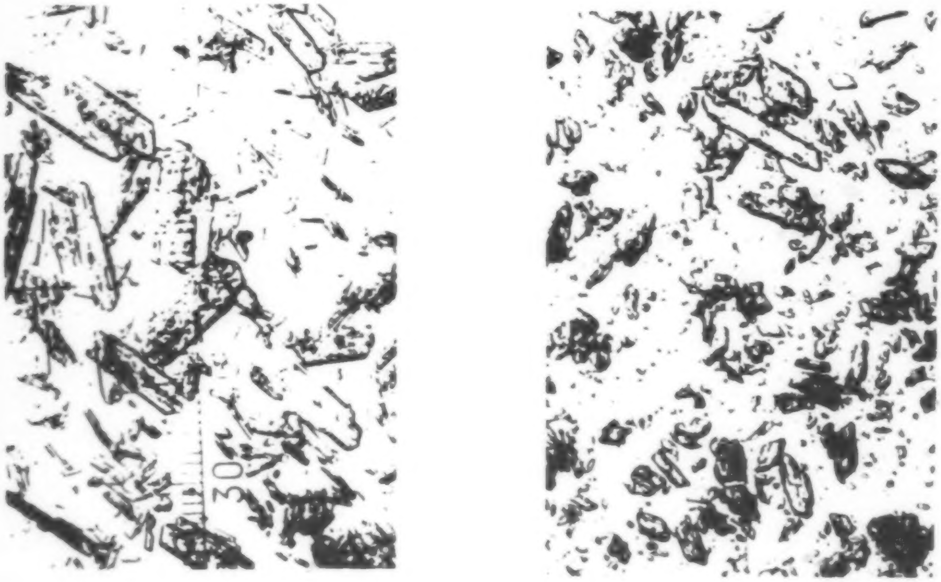
(H) $CaCO_3$ scrubbing,(Babcock-Hitachi, Chugoku Electric)

Figure 6-4 (continued). Photomicrograms of by-product gypsum.



(I) $Na_2SO_3$-$CaCO_3$ process
(Showa Denko, Chiba)

(J) $Na_2SO_3$-$CaCO_3$ process
(Kureha-Kawasaki, Tohoku Electric, Shinsendai)



(K) $(NH_4)_2SO_4$-$Ca(OH)_2$ process
(Nippon Kokan, Keihin)

(L) $(NH_4)_2SO_4$-$Ca(OH)_2$ process
(Kurabo, Hirakata)

Figure 6-4 (continued). Photomicrogram of by-product gypsum (x100).

The by-products are nearly white or light brown. Most of the wet process plants in Japan incorporate a cooler or a prescrubber, where the gas is sprayed with water for cooling as well as for humidifying and removing most of the dust that has not been caught by an electrostatic precipitator. There is a recent trend toward simplifying the process by reducing the size of the cooler and discharging the dust-containing liquor from the cooler to the scrubber without filtration. The dust goes into gypsum, which is then fairly colored. Users of gypsum for cement and wallboard have gradually become accustomed to the colored product because the small amount of dust derived from the oil-fired flue gas passed through an electrostatic precipitator has no adverse effect. The gypsum obtained at the new plant of Mitsui Aluminum Co. from a coal-fired flue gas by the Mitsui-Miike process contains about 5 percent fly ash, which is acceptable. The gypsum to be obtained at Isogo plant, EPDC, by treating a flue gas from low-sulfur coal will contain much more fly ash and may be useless not only for board but also for cement.

The thickness of gypsum crystals is generally an important factor in the strength of wallboard. Crystals obtained from the wet-limestone processes (Figure 6-4, F and H) are not very long but have considerable thickness and are ideal for use in wallboard.

For use as a retarder in cement setting, gypsum should contain less than about 10 percent moisture because wet gypsum tends to form a "bridge" in the hopper and cannot be charged smoothly to the cement mill. Normally the by-product gypsum contains less than about 10 percent moisture after being centrifuged. Well-grown gypsum crystals produced by some of the indirect limestone processes (100 to 500 microns; Figure 6-4, I and M) contains only 5 to 7 percent moisture after being centrifuged. The presence of sodium in gypsum can adversely affect the property of cement but the amount of sodium in gypsum produced by the sodium-limestone process is negligible because of the simplicity of washing due to the large crystal size. Fly ash, about 10 percent in gypsum, has no ill effects. Calcium sulfite can be used also for a retarder in cement setting, replacing a portion of the gypsum. Magnesium sulfate and calcium chloride in amounts less than 0.5 percent may have no ill effects on board and cement production.

### Gypsum for Building Material

Because a considerable oversupply of gypsum may occur in the future, many groups are investigating new uses of gypsum. The most promising new use is as a building material. The usual type of calcium sulfate hemihydrate ($\beta$ type) has lower strength than concrete (Figure 6-5). The hemihydrate of $\alpha$ type has a much larger crystal size and higher strength than $\beta$ type but is fairly expensive. The form II anhydrite, which is obtained by heating gypsum at 950 to 1000°C, hydrates fairly rapidly and increases in strength when a small amount (1 to 2 percent) of potassium sulfate is added. Recent tests by Onoda Cement Co. have shown that an anhydrite of good quality can be obtained with by-product gypsum from $SO_2$ recovery if the fly ash content is less than about 5 percent. A larger amount of fly ash tends to decrease the strength.

Technology for reinforcement of gypsum with glass fiber has been developed recently in England.[10] The reinforced gypsum from $\alpha$ type hemihydrate has compression, bending, and tensile strengths equal to and an impact strength higher than asbestos-reinforced concrete.

### Gypsum Plastic Composite

An important defect in gypsum as a building material is its lack of resistance to water. To eliminate this weakness, a gypsum plastic composite (GPC) has been recently developed in Japan through the cooperation of Mitsui Toatsu Chemical and Taisei Construction Co. (Figure 6-6). Usually

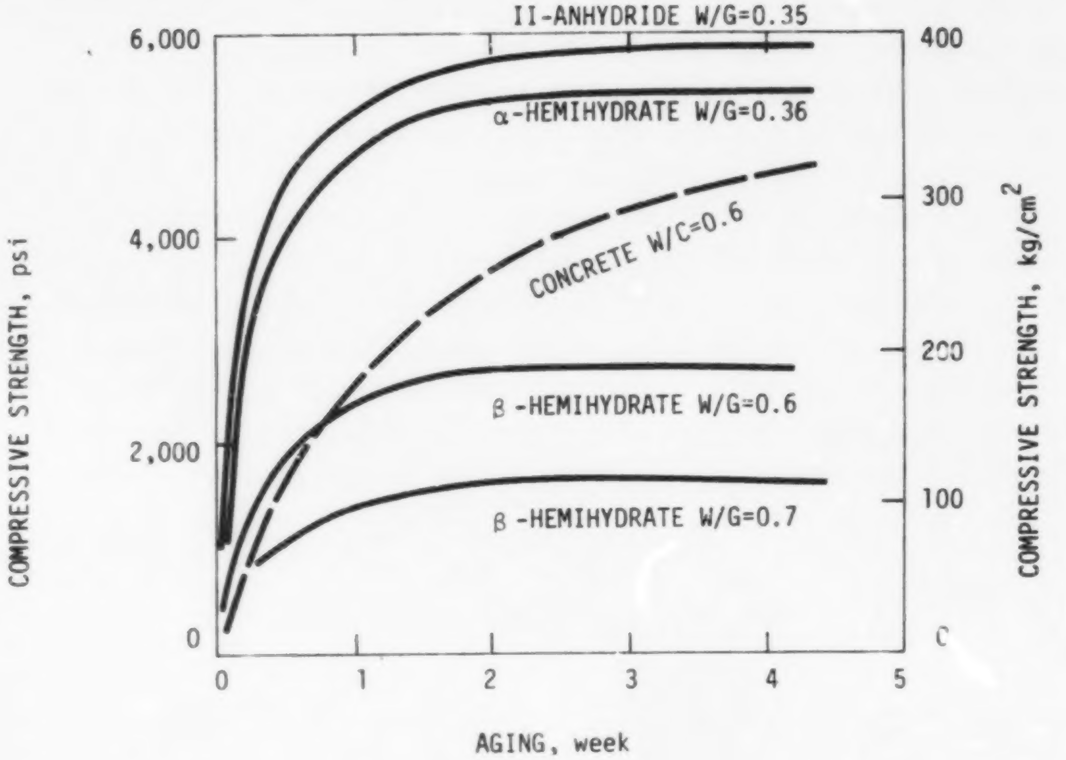


Figure 6-5. Strength of various types of gypsum and concrete (W/G and W/C mean weight ratio of water against gypsum and cement, respectively).

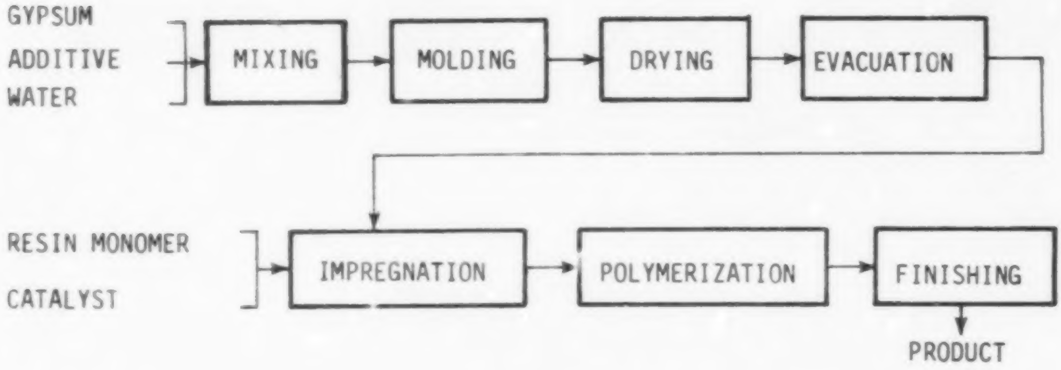
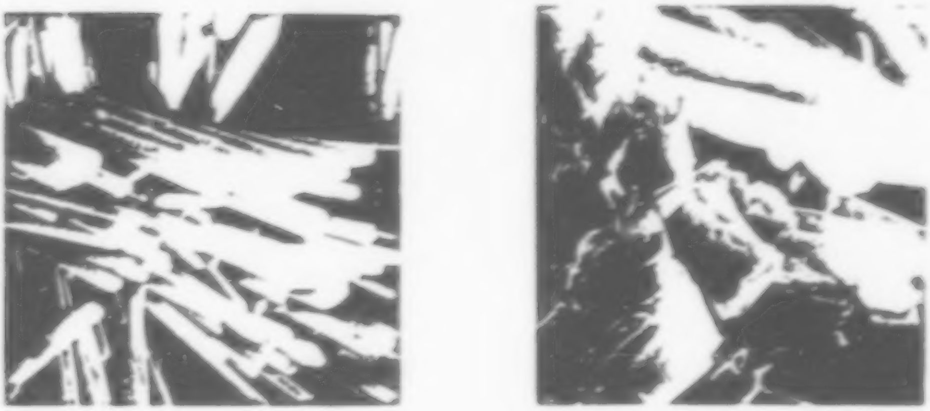

GYPSUM
ADDITIVE
WATER
MIXING
MOLDING
DRYING
EVACUATION
RESIN MONOMER
CATALYST
IMPREGNATION
POLYMERIZATION
FINISHING
PRODUCT

Figure 6-6. Process for GPC production.

a resin monomer such as methyl methacrylate (MMA) or styrene is used for impregnation. The monomer is polymerized by a thermal catalytic means. Some results of tests with MMA are shown in Tables 6-3 and 6-4. GPC has superior strength, resistance to water, acid and base, and also good workability and semi-incombustible property. It may, therefore, be used as a high-grade building material.

Observations of the broken surface of pieces of ordinary gypsum and GPC by a scanning-type electron microscope have shown that for gypsum, crystals were not broken but came apart from each other by stress (Figure 6-7), whereas for GPC, each crystal was broken, requiring a great stress. This explains the high strength of GPC.



(M) Gypsum

(N) GPC

Figure 6-7. Scanning-type electron photomicrograms of broken surface (x 1500).

Table 6-3. BLENDING OF MATERIALS

| No. | β-hemihydrate | Glass fiber | Water | MMA |
|---|---|---|---|---|
| A | 100 | 0 | 57 | 0 |
| A' | 100 | 0 | 57 | 35.5 |
| B | 100 | 3 | 63 | 0 |
| B' | 100 | 3 | 63 | 38.1 |

Table 6-4. PROPERTIES OF GYPSUM AND GPC

| No. | Specific gravity, G/ml | Compressive strength, kg/cm$^2$ | Bending strength, kg/cm$^2$ | Wearing, mm/1000 revolutions |
|---|---|---|---|---|
| A | 1.274 | 132 | 52 | 8.0 |
| A' | 1.699 | 720 | 196 | 0.8 |
| B | 1.214 | 99 | 68 | 20.0 |
| B' | 1.663 | 790 | 274 | 1.0 |

# 7. COMPARATIVE EVALUATION

In this section the various FGD processes are considered with specific reference to (1) their output and treatment of wastewater and (2) their capital and operating costs. A technical evaluation of the major process categories follows, with discussion of their potential for application in the United States.

## WASTEWATER

As shown in Table 7-1, most Japanese FGD plants purge wastewater, mainly to prevent the accumulation of impurities in the circulating liquor. One of the impurities is chlorine, which is derived from fuel and process water. The accumulation of chlorine causes corrosion. Magnesium is derived from lime or limestone and interferes with the reaction of sodium sulfite and limestone.

In the Wellman-Lord process, sodium sulfate and thiosulfate accumulate and disturb $SO_2$ absorption. The amount of wastewater from the Nishinagoya plant using the Wellman-MKK process is relatively small but the water requires extensive treatment because it contains reducing compounds. Wastewater from processes by-producing gypsum contains essentially no reducing compounds because the processes include an oxidation step; the wastewater can be treated by simple neutralization and filtration.

The Mitsubishi-JECCO process gives less wastewater than do others; the water ratio ranges from 0.37 to 0.64 (Table 7-1). The Chiyoda process gives more wastewater because it uses an acid as the absorbent, which makes it necessary to

## Table 7-1. WASTEWATER FROM FGD PLANTS (OIL-FIRED BOILERS)

| Process | User | Plant site | Capacity, MW[a] | Inlet $SO_2$ ppm | Waste-water t/hr (A) | Gypsum, t/hr |  | Water ratio A+C (A+B+C) | Waste-water, kg/MW-hr |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Solid (B) | Moisture (C) |  |  |
| Mitsubishi-JECCO | Kansai Electric | Kainan | 150 | 270 | 1.5 | 0.9 | 0.1 | 0.64 | 10 |
| Mitsubishi-JECCO | Kyushu Electric | Karita | 175 | 800 | 2.9 | 2.9 | 0.3 | 0.52 | 17 |
| Mitsubishi-JECCO | Chubu Electric | Owase[a] | 750 | 1,400 | 14.0 | 29.0 | 2.9 | 0.37 | 19 |
| Babcock-Hitachi | Chugoku Electric | Mizushima | 105 | 400 | 4.0 | 0.9 | 0.1 | 0.82 | 34 |
| Chubu-MKK | Ishihara Chemical | Yokkaichi | 85 | 1,300 | 4.4 | 2.2 | 0.2 | 0.67 | 47 |
| Showa Denko | Showa Denko | Chiba | 150 | 1,400 | 3.5 | 5.2 | 0.5 | 0.45 | 33 |
| Chiyoda | Daicel Co. | Aboshi | 31 | 1,400 | 2.0 | 1.0 | 0.1 | 0.68 | 64 |
| Chiyoda | Hokuriku Electric | Toyama | 250 | 610 | 15.0 | 7.5 | 0.7 | 0.73 | 60 |
| Wellman-MKK | Chubu Electric | Nishinagoya | 220 | 1,800 | 3.0 |  |  |  | 14 |

[a] Designed value; the plant is under construction.

keep the chlorine content lower for prevention of corrosion. Wastewater can be reduced by using a material with greater corrosion resistance, but this would increase the capital cost.

Many states in the U.S.A. prohibit the discharge of wastewater but allow the discarding of calcium sulfite sludge, which normally contains about 50 percent water. The water ratio is about 0.5 in this case, about the same as in the Mitsubishi-JECCO and Showa Denko processes.

It has been argued that the purge of wastewater in Japan may be one of the important factors contributing to scale-free operation, because the degree of saturation of the scrubber liquor might be lowered by adding much fresh water. A calculation based on operational data, however, shows that the ratio of the flow rate of purge stream and scrubber liquor is only about 1 to 1500 for the Mitsubishi-JECCO process, an indication that the small amount of purge water may not be significant for the degree of saturation.

Two commercial plants using the wet process have not purged any wastewater yet. One of them, which went into operation in January 1974, is the Shinsendai plant, Tohoku Electric, using the Kureha-Kawasaki sodium-limestone process. The plant is equipped with a facility for removing magnesium from the circulating liquor. The chloride content has gradually increased and has reached 7000 ppm in the liquor; some tendency for corrosion has been manifest. Chloride is leaving the system with gypsum which has 6 to 7 percent moisture. It seems that the chloride input and output have been almost equalized at the 7000 ppm concentration.

Another plant that has not purged wastewater is the Okayama plant, Dowa Mining, which went into operation in September 1974 using the Dowa aluminum sulfate-limestone process. Magnesium in the liquor has increased, but chloride has not increased appreciably. The plant treats tail gas from a sulfuric acid plant, which may contain less chloride than does flue gas. Moreover, the gas temperature is lower and less input water is needed. In the long run, removal of magnesium and chloride may be required, particularly for the treatment of flue gas.

The Amagasaki plant Kansai Electric Power, which is based on the Mitsubishi-JECCO lime process, operated for the first three months without any wastewater. As chloride content of the liquor increased substantially, plant operators started to purge some water (after being treated) to lower the chloride concentration. It may be more practical to purge some water after treating it than to install additional facilities for magnesium removal and to use expensive corrosion-resistant materials.

Many of the plants with dry absorption processes have wet systems after the absorption and are not free from wastewater. Both the Kashima plant, Tokyo Electric, using the Hitachi carbon process, and the Yokkaichi plant, Showa Yokkaichi Sekiyu (SYS), using the Shell process, have purged more wastewater than do some of the plants listed in Table 7-1.

## ECONOMICS

The investment cost for an FGD plant is lowest with a simple sodium scrubbing process that by-produces sodium sulfite. The demand for the sulfite, however, is limited, and further notable development of the process cannot be expected. Among other FGD processes, the wet-lime/limestone process requires the least investment cost. The cost for a unit with a capacity of 450,000 to 750,000 Nm$^3$/hr (150 to 250 MW) was $25 to 30/kW in early 1973 and is $60 to 65/kW at present. The cost for indirect lime/limestone processes is estimated to be 5 to 30 percent higher. The Dowa process may entail the least capital investment among the indirect processes because of its simplicity and the requirement for relatively small vessels. The Kureha-Kawasaki sodium-limestone process seems most costly because it requires many vessels, including one for removal of magnesium from the circulating liquor; the process is advantageous however, in that no wastewater is purged. The Wellman-Lord process seems to be as costly as the Kureha-Kawasaki process because it requires many units of equipment for wastewater treatment. The investment cost for the dry processes could be even more than for the Kureha-Kawasaki and Wellman-Lord processes because dry processes require large absorbers and relatively complicated systems for treatment of the absorbed $SO_2$.

The operating costs are also the lowest for the wet-lime/limestone process and may be the highest with some of the dry processes that consume a reducing gas such as hydrogen.

For a new FGD unit with a capacity of 450,000 to 750,000 $Nm^3$/hr, the desulfurization cost including the running and fixed costs (depreciation for 7 years) would be $17 to 20/kl oil (about 4.5 mil/kWhr) for wet-lime/limestone process and about 30 percent more for expensive processes. Two years ago, the cost was $5 to 7/kl oil, while the price difference between low- and high-sulfur oils was also $5 to 7/kl. At present, the price of low-sulfur oil is $25 to 30 more per kiloliter than that of high-sulfur oil (Table 2-3), and the big difference is encouraging the construction of many FGD and HDS (hydrodesulfurization) plants.

Thermal electric power generation costs about 2 cents/kWhr at present and FGD adds 20 to 30 percent to the power cost. This high energy cost has started to affect the Japanese economy. Oversupply of FGD by-products - sodium sulfite, sulfuric acid, and gypsum - is inevitable and will cause additional difficulty (Figures 6-1 and 6-2). By-production of elemental sulfur from FGD will become more important in Japan as in the U.S.A. However, the sulfur-by-producing FGD processes are very costly except for oil refineries already equipped with Claus furnaces. The HDS of oil might be a better way for sulfur by-production.

Generally speaking, the manufacturers and users of FGD plants in Japan tend to prefer excessively elaborate systems and to install deluxe plants in order to ensure smooth automatic operation under variable conditions and to obtain very high $SO_2$ recovery and clean by-products. This tendency may have been induced by the fact that the authorities allow the FGD cost to be added to the cost of the product - power cost for power companies, for example - while in many states in the U.S.A. this is not allowed. The process developers and plant constructors should make further efforts to simplify the processes and to reduce construction costs.

## TECHNICAL EVALUATION

### Dry Processes

Until several years ago the dry processes were considerably more promising than the wet processes because no reheating of the gas is required and also because of possible elimination of wastewater. In practice, however, most dry processes include a wet process for treatment of the recovered $SO_2$ and thus are not free from wastewater. The advantage that no reheating is required cannot compensate for the disadvantages - the need for a large absorber and regeneration facility and the use of an expensive absorbent or reducing agent.

Chubu Electric Power abandoned its prototype plant (130 MW) based on the activated manganese process after operating it for about 2 years.

Although other plants based on the dry process are being operated and a few other processes are being tested, there are no plans to build more plants with the dry process.

Very recently another advantage of the dry process has been recognized in connection with flue gas denitrification, for which a selective catalytic reduction at 300 to 350°C appears promising. As the catalyst for the reduction tends to be contaminated by $SO_3$, $SO_2$, and dust in flue gas, those should be minimized prior to the reduction. The wet process is not favorable because much reheating of the gas is needed. To reduce the temperature adjustment, it may be preferable to treat the hot gas at about 350°C from the boiler with a high-efficiency hot electrostatic precipitator, a dry-process desulfurizer, and a denitrification unit, and then send the gas into an air preheater. The high-efficiency hot electrostatic precipitator is expensive, but such a system may be used if regulations requiring flue gas denitrification are enforced.

### Wet Lime/Limestone Process

Wet lime/limestone processes are most promising in Japan, as in the United States. The main difference is that in Japan virtually all of the by-product is oxidized into gypsum, except at the Omuta plant, Mitsui Aluminum Co.

The Mitsubishi-JECCO process has been most widely used because of its reliability and low energy consumption. "Saturated operation" without scaling problems has been achieved in contrast to the "unsaturated operation" at the Paddy's Run station of Louisville Gas and Electric and at the Omuta plant. Most plants based on the Mitsubishi-JECCO process have so far treated gases with low $SO_2$ concentration (300 to 800 ppm) except for a plant of Onahama Smelter, which treats gas containing 15,000 to 25,000 ppm $SO_2$. Operation of many larger plants now under construction to treat flue gas with higher $SO_2$ concentration will allow further evaluation.

The Chemico-Mitsui process also gained much fame from successful operation of the Omuta plant treating coal-fired flue gas. There has been much argument concerning the reason for the scale-free operation. In addition to the "unsaturated operation," careful control seems to be the key to success. For example, the pH of the slurry is being measured manually because an automatic pH meter might not be quite as reliable. The Mitsui-Miike process has an advantage in that it achieves high $SO_2$ removal with limestone and effects pH control without sulfuric acid, similarly to the two-tower system of the Mitsubishi-JECCO process. Those processes would be useful also in the U.S.A. provided that the by-product gypsum can be utilized.

Operation of the Mizushima plant, Chugoku Electric Power, using the Babcock-Hitachi process has been carried out smoothly for several months. Further evaluation of the process and of other wet lime/limestone processes will require longer operation of larger plants.

### Indirect Lime/Limestone Process

Among the double-alkali-type processes, the Chiyoda process and the sodium-limestone processes of Showa Denko and Kureha-Kawasaki have been widely employed, presumably because of their good performance and use of limestone. The Chiyoda process is simple and plant operation is most easy, although it requires a big absorber and a high L/G ratio. Operation of a pilot plant of Gulf Power Co. in Florida, which will commence shortly using the Chiyoda process, will allow evaluation of the applicability to flue gas from coal-fired boilers.

The sodium-limestone processes are rather complicated because they include a sodium sulfate decomposition step. The processes require large land space and relatively high investment cost. On the other hand, sodium consumption is low - about one-fifth that required for a Wellman-Lord process plant of equal capacity that does not use an oxygen inhibitor.

The Dowa aluminum sulfate process seems promising because of its simplicity of operation at a relatively low L/G ratio, and use of limestone. The process may be useful not only for tail gas but also for flue gas. Both the NKK and Kurabo processes use ammonia scrubbing and can produce either gypsum or ammonium sulfate. NKK uses an ammonium sulfite solution at pH 6 with an L/G ratio of 2. Plume formation is the main problem for this type of ammonia scrubbing. Recently a technique for plume prevention has been developed by Catalytic Co., U.S.A., jointly with TVA using a precise adjustment of the composition of liquors in three or four stages in the scrubber. Such fine control may not be carried out easily for the treatment of waste gas from a sintering plant, whose flow rates and $SO_2$ concentrations fluctuate very frequently.

The Kurabo process uses an ammonium sulfate solution of pH 3.5 to 4.0 and is essentially free from plume problems although a high L/G ratio (about 8) is required. This process might be advantageous in districts where plume emissions are severely restricted. On the other hand, the NKK process may be advantageous for ammonium sulfate production because the concentration of the absorbing liquor is higher, and less energy is needed for crystallization.

Generally, the indirect processes are 5 to 30 percent more expensive than the wet lime/limestone processes but are safer with respect to scaling problems. Double-alkali processes using sodium scrubbing are costly because they require a desulfation step. As investigators continue to improve the technology for wet lime/limestone processes, expensive indirect processes may not be used widely unless regulations are tightened to require more than 97 percent $SO_2$ removal, for which the sodium processes are advantageous. Indirect processes that use acid or acidic solutions may be useful for plants where precise control of the operation is difficult.

## Other Wet Processes

Among other processes, the Wellman-Lord (W-L) process has been used widely in Japan because of its smooth operation and of the short supply of sulfuric acid caused by the shutdown of several old acid plants that used pyrite as raw material. The major problem for the process is the wastewater, containing sodium sulfate, sulfite, and a small amount of thiosulfate. With the increasing severity of wastewater regulations, the difficulty of wastewater treatment for the W-L process is becoming apparent. The use of an oxidation inhibitor by SCEC to reduce the formation of sulfate and the amount of wastewater increases the difficulty of removing the COD (chemical oxygen demand) in the water.

The magnesium scrubbing process, which also produces sulfuric acid, needs fuel for calcination whereas the W-L process requires steam. For the magnesium process, wastewater is no problem, but plant operation may not be as satisfactory as with the W-L process. With further improvement, the magnesium process could be advantageous for sulfuric acid production; the W-L process may be more suitable for by-production of elemental sulfur because of the high concentration and purity of the regenerated $SO_2$.

In Japan, gypsum, sulfuric acid, sodium sulfite, etc. have been considered more valuable by-products than sulfur. Thus, Japanese industry has shown little or no interest in sulfur-producing FGD processes. However, as the supply of these former products begins to exceed the demand, more effort will likely be concentrated on the development of sulfur-generating FGD processes.

## POTENTIAL FOR APPLICATION IN THE U.S.A.

### Differences Affecting Process Application

Several considerable differences in circumstances in the U.S.A. and Japan affect the feasibility of applying the Japanese processes.

(1) In the U.S.A., gypsum and sulfur from natural sources are plentiful and cheap, whereas these materials are scarce in Japan. By-products from desulfurization can be sold for a good price in Japan, a fact conducive to the development of recovery processes.

(2) In the U.S.A., most plants have enough space to abandon waste products, whereas in Japan the space limitations necessitate maximum utilization of by-products.

(3) In the U.S.A., about 60 percent of the electric power is generated by burning coal, which gives much fly ash. In Japan most power plants burn oil, which gives little fly ash or dust. This is an advantage for recovery of by-products with high purity.

(4) In the U.S.A., many power plants are located far from chemical plants. In Japan power and chemical plants are usually close to each other; hence it is easy for chemical plants to utilize desulfurization by-products and for power plants to use chemicals.

(5) In Japan many plants are close to cities. More than 90 percent removal of $SO_2$ or less than 100 ppm $SO_2$ in emitted gas is usually required. In the U.S.A. about 80 percent desulfurization or 300 ppm $SO_2$ in the gas is usually acceptable.

(6) Regulations of the purge of wastewater in many states in the U.S.A. are more stringent than in Japan.

These differences strongly affect the types of processes to be used and design of the plants. Any Japanese process to be applied in the U.S.A. should be modified to suit local conditions. For example, wastewater should be minimized or eliminated, while prescrubbers and scrubbers can be smaller.

### Possibility of Gypsum Production in U.S.A.

FGD processes producing gypsum are highly advanced and widely used in Japan, while in the U.S.A. throwaway calcium sulfite processes are common. The author envisions a possibility for the U.S.A. to generate a considerable amount of by-product gypsum in the future. At present the U.S.A. imports about 6 million tons of gypsum yearly.

It is natural that U.S. producers of cement and wallboard should be reluctant to use the by-product because they have no experience with it and are concerned about possible difficulties. The situation was the same in Japan about 10 years ago: the cement and wallboard producers started to use phosphogypsum - the by-product of phosphric acid production from phosphate ore as shown in Figure 6-4 B and C - only after they were forced to do so by a shortage of natural gypsum. They have gradually realized that by-product gypsum is useful and reliable. FGD gypsum is better than phosphogypsum because it contains no harmful impurities such as phosphoric acid and fluorine, which can affect the quality of cement and wallboard. Japanese producers no longer hesitate to use FGD gypsum.

Many Japanese FGD plants use sulfuric acid to lower the pH of calcium sulfite slurry so as to promote the oxidation into gypsum, but this may not be convenient in most plants in the U.S.A.

Sulfuric acid may be unneeded with a two-absorber system, in which the pH of the discharged slurry can be lowered to a suitable level for the oxidation. Installation of the additional absorber, oxidizer, and centrifuge required for gypsum production would add 40 to 50 percent to the investment cost of the plants with conventional throwaway sludge process. Yet the advantage to be gained might offset the additional expenses in some districts in the U.S.A., where imported gypsum is used for cement or wallboard production or where no land is available for sludge disposal.

Gypsum also offers an advantage as a throwaway material. Gypsum may be piled up to 100 feet high, as is done at phosphoric acid plants in Florida, and thus allows great saving of land space as compared with the use of calcium sulfate sludge ponds.

Wastewater

In many states in the U.S.A. wastewater discharge is prohibited, whereas in Japan most FGD plants purge some water after treating it. When no water at all is discharged from the system, impurities derived from fuel and process water will accumulate in the circulating liquor and cause trouble. Discarding of sludge, which usually contains about 50 percent water, also disposes of considerable amounts of the impurities and may prevent their accumulation in significant amounts. When gypsum that contains less than 10 percent moisture is discharged without any wastewater, the chloride concentration in the liquor would normally reach 5000 to 30,000 ppm, depending on the chlorine content of fuel and process water. Although the high concentrations of chlorine may not increase scaling in "saturated operation" as it may in "unsaturated operation," they will promote corrosion and necessitate the use of corrosion-resistant materials. It might be feasible for U.S. plants to purge a small amount of water after giving proper treatment, including the removal of heavy metals and other undesirable components.

# REFERENCES

The process descriptions in this report are based primarily on the author's visits to the desulfurization plants, his discussions with the users and developers of each process, and data made available by them. In addition, the following publications were used and are cited as references.

1. The Petroleum Industry in Japan 1973, The Japanese National Committee of the World Petroleum Congress (Mar. 1974)

2. Borgwardt, R.H. EPA/RTP Pilot Studies Related to Unsaturated Operation of Lime and Limestone Scrubbers, EPA FGD symposium (Nov. 1974 in Atlanta)

3. Ando, J. Recent Developments in Desulfurization of Oil and Waste Gas in Japan (1973) EPA-R2-73-229, Office of Research and Monitoring, U.S. EPA, Washington, D.C. (May 1973)

4. Atsukawa, M., K. Matsumoto, et. al., Removal of $SO_2$ from Flue Gas by Wet Process, Mitsubishi Heavy Industries Report (Mar. 1974)

5. Elder, H. W., F. T. Princiotta, G. A. Hollinden and S. J. Gage, Sulfur Oxide Control Technology, Visits in Japan--August 1972, U.S. Government Interagency Report, Muscle Shoals, Alabama (Oct. 30).

6. Yoshida, S., Chemical Economy and Engineering Review, Vol. 6, No. 3, pp 37-42 (Mar. 1974)

7. Noguchi, M., Status of the Chiyoda Thoroughbred 101 Process, EPA FGD symposium (Nov. 1974)

8. Hollinden, G. A. and F. T. Princiotta, Sulfur Oxide Control Technology, Visits in Japan--March 1974, U.S. Government Interagency Report (Oct. 1974)

9. Kawaguchi, K., The Largest Stack Gas Desulfurization Plant, 220 MW Full Scale at Chubu Power (JAPAN) Nishi-Nagoya Plant by Wellman-Lord Process, Thermal and Nuclear Power Vol. 25 No. 208 (1973)

10. Ali, M. A. J., Material Science, 4(5), p. 398 (1969)

11. Ploeg, J. E. G., E. Akagi, and K. Kishi, "Shell's Flue Gas Desulfurization Unit at Showa Yokkaichi Sekiyu K. K. "Petroleum International, Vol. 14, No. 4 (July 1974)

12. Pohlenz, J. B., "The Shell Flue Gas Desulfurization Process" EPA FGD Symposium (Nov. 1974, in Atlanta)